THE REMOVAL OF FUEL OIL COMPOUNDS FROM GROUNDWATER FOR POTABLE SUPPLY

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October 2004.

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Abstract.

This study was a joint project between the Environmental Engineering Group of the Department of Civil and Environmental Engineering - University College London and Anglian Water. The project was funded by an EPSRC CASE studentship (award No. 00800074) with Anglian Water.

Cases of fuel oil contamination of groundwater are common throughout the world. The leakage of above and below-ground fuel storage tanks pose a significant threat to groundwater and in some cases potable water supply (PWS) boreholes. Although in-situ remediation methods are fundamental to a remediation strategy and can remove large amounts of hydrocarbon contamination, practical steps must sometimes be taken at PWS boreholes down-gradient of the contamination source to protect the supply.

This study details the optimisation of a modular post-abstraction remediation system incorporating air-stripping and granular activated carbon (GAC) technologies. Emphasis throughout the experimental phase of the study is placed on methyl-tertiary-butyl-ether (MTBE) and benzene, toluene, ethylbenzene and xylene (BTEX) compounds. MTBE and BTEX compounds represent those most likely to reach the borehole after a contamination event, and also those which pose the greatest risk to human health.

Stringent remedial targets were implemented, based upon world-wide drinking water standards. For benzene the remedial target was 1μg/L and for MTBE the remedial target was 5μg/L.

Utilising high performance stainless steel structured packing with air-to-water ratios ranging from 9 – 86, air-stripping removal efficiencies for MTBE ranged from 20 – 89%, whilst removal efficiencies for benzene ranged from 52 – 90%.

The results of the study suggested that the removal efficiency of MTBE was dependent upon the air-to-water ratio, whilst the removal efficiency of benzene was independent of the air-to-water ratio.

Utilising F400 GAC, the total adsorptive capacity for MTBE was 3.45 mg/g, whilst the adsorptive capacity for benzene was 2.72 mg/g. However, the general results suggested that benzene was adsorbed much more readily than MTBE.

Utilising F600 GAC, the total adsorptive capacity for MTBE was 1.45 mg/g, whilst the adsorptive capacity for benzene was 1.96 mg/g.

The results suggested that the adsorptive capacity was dependent upon the influent concentration and that benzene was preferentially adsorbed ahead of MTBE.

Note that throughout this study the term 'fuel oil' has been used as a generic term to describe all types of fuels (i.e. gasoline, diesel, central heating fuel oil etc). The term can also imply a specific (heavy) fuel with an alkane carbon range nC_{12}-nC_{34}.

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CHAPTER 1: LITERATURE REVIEW.

The aim of Chapter 1 is to review the literature relating to the fuel oil contamination of groundwater. The findings of the literature review are then used to formulate the experimental phase of the project in Chapter 2.

1.1. Fuel Oil Contamination of Groundwater: Current View.

The aim of this section of the literature review chapter is to introduce current issues related to the fuel oil contamination of groundwater. The causes and implications of groundwater contamination are discussed. Implications include those to the natural environment and to human health. Relevant legislation on fuel storage and drinking water standards are reviewed.

1.1.1. Availability of Information.

Information with regards to the recent contamination of groundwater sources is sometimes hard to come by. Detailed in this section are some of the organisations used within the study as a source of information and data. Information relating to case studies on specific contamination events and clean-up operations by respective organisations is not widely published. This is due to the sensitive nature of the subject. Petrochemical companies protect the specific breakdown of their fuels in order to prevent competitors gaining information on their products. With respect to the issue of the fuel oil contamination of groundwater, a breakdown of the contaminant is a vital step in producing remedial strategies.

The UK Environment Agency (EA) is probably the largest and most easily accessible source of information with regards to the subject within the UK. The EA is the regulator that overseas the protection of the environment within England and Wales. As the regulatory body the EA provides legislation and guidelines relevant to groundwater contamination by fuel oils. The EA monitors organisations with respect to the legislation, and has the power to take parties to court if the law is not adhered to. The Drinking Water Inspectorate (DWI) is the body responsible for assessing the quality of drinking water in England and Wales. It also has the power to take enforcement action if standards are not being met, or when drinking water is not fit for human consumption. The DWI website also serves as a source of information relating to the fuel oil contamination of groundwater. In Scotland, all environmental issues are dealt with by the Scottish

Environmental Protection Agency (SEPA). The British Geological Society (BGS) provides a large library of technical information related to groundwater contamination. With respect to the science of the remediation technologies employed, the advent of online e-journals has provided a vast database of journals, papers, policy debates and research articles on the subject. This information is freely available on the World Wide Web.

The US has a vast resource of related science, case studies and policy issues regarding the fuel oil contamination of groundwater, perhaps indicating the size of the problem they have experienced over the past 2 decades. The US Environmental Protection Agency (USEPA) has a dedicated resource relating to groundwater issues. Indeed most of the literature relating to remediation technologies comes from US based journals.

1.1.2. Groundwater Sources for Potable Supply.

Groundwater supplies 30% of all water abstracted for public supply in England and Wales, 8% in Northern Ireland and 5% in Scotland (DETR/ DWI Publication Crypotsporidium in Water Supplies, 2000). Regional differences between groundwater abstraction are due to the distribution of aquifers within the UK, and the fact that geographical conditions support the use of surface water abstraction in both Northern Ireland and Scotland, rather than groundwater abstraction. In comparison, groundwater supplies approximately 78% of drinking water to community water systems within the US (USEPA, 2003). This represents a high reliance on groundwater as a drinking water source in the US.

Reliance on groundwater sources varies with regions in the UK. For example, Groundwater amounts to 80% of the total public water supply in the South-East of England. In the Severn and Trent basins, Eastern England, Thames Valley and the Wessex Regions, groundwater abstraction varies from 30-50% of total water supplied to the public. Total abstraction within the UK, including that used by industry and agriculture is 2400-million m^3/ year. 85% of this groundwater is supplied from the Chalk and Permo-Triassic sandstone aquifer systems. Figure 1.1 details major UK aquifers.

Figure 1.1. Major UK Aquifers. Source: EA.

Figure 1.2 details aquifers found within the Anglian geographical region of the UK.

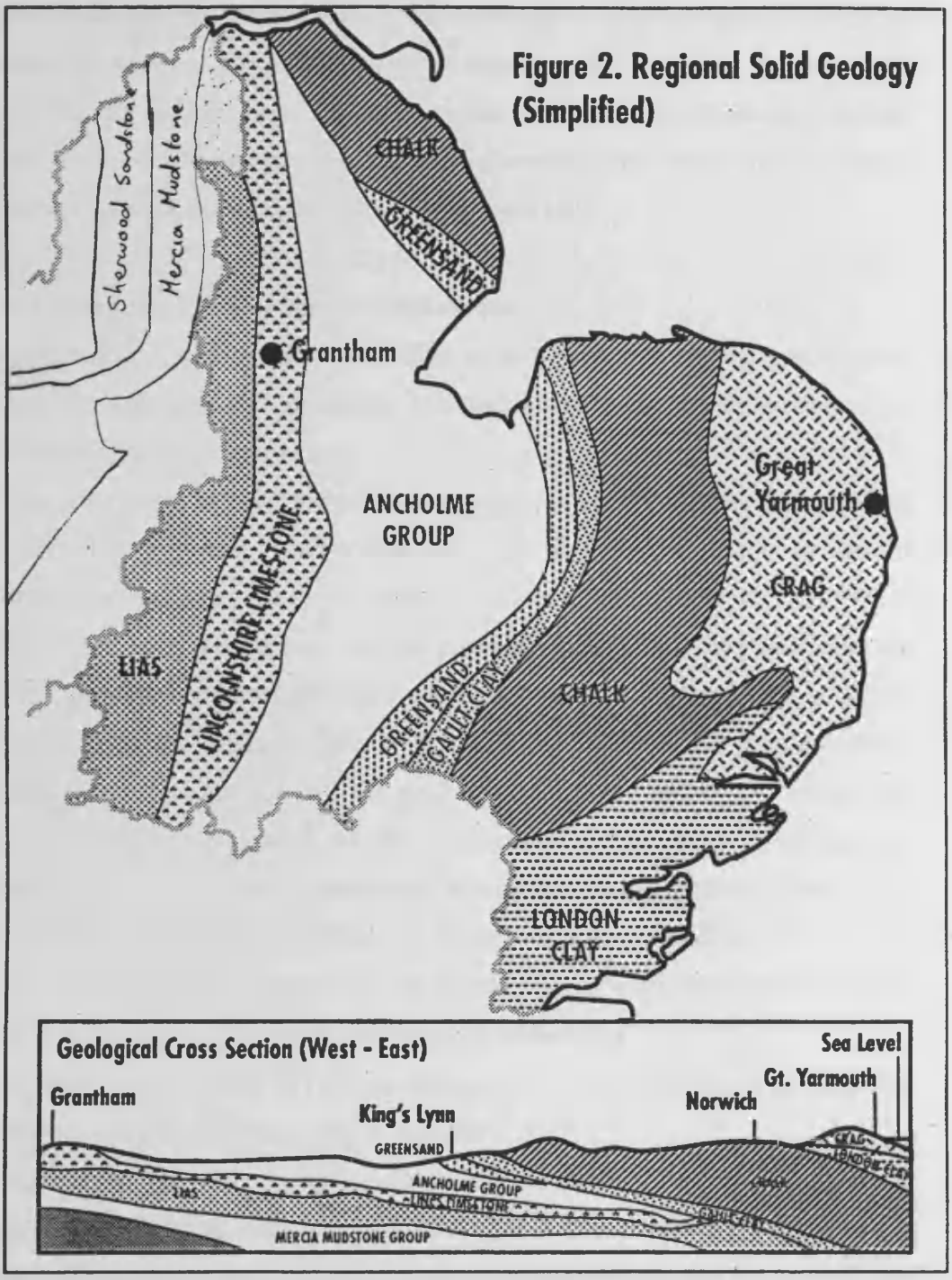


Figure 1.2. Major Aquifers within the Anglian Region. Source: Anglian Water.

The EA has new powers under the Groundwater Regulations 1998, which are necessary to fully transpose the EU Groundwater Directive (80/68/EEC) into UK law (EA, 1999). The regulations state that petroleum must not enter groundwater.

These regulations are likely to have a major impact on the storage of petroleum based substances.

The EA has defined groundwater Source Protection Zones (SPZs) to provide an indication of the risk to groundwater supplies after possible contamination incidents. SPZs have been assigned approximately 2,000 groundwater sources used for public drinking water supplies. Generally, the closer the activity or release is to a groundwater source the greater the risk.

1.1.3. Groundwater Contamination Sources.

It goes without saying that every effort must be taken to protect groundwater resources from harmful substances. This will protect not only the environment, but drinking water sources also.

There have been many high profile examples of the petroleum contamination of groundwater over the past two decades. This is reflected in the amount of literature published on the causes of and remediation of contaminated aquifers.

One of the most recent high profile cases of groundwater contamination by petroleum-based hydrocarbons has been the pollution of Californian groundwater sources with the fuel additive methyl-tertiary-butyl-ether (MTBE). Initially added to gasoline to improve the performance of the fuel and to reduce the amount of unburnt hydrocarbons released into the atmosphere, the compound has contributed to widespread groundwater and drinking water contamination in the US. The problem has been caused by the large amounts of MTBE added to US fuel, coupled with the compound's unique chemical and physical characteristics. The health effects of MTBE are not yet fully understood.

The global production of MTBE has climbed to over 20 million tons per year and that it is used almost exclusively in gasoline.

Other compounds such as benzene, toluene, ethylbenzene and xylene (commonly termed BTEX compounds) have great environmental and health significance. As with MTBE, this is largely due to their chemical and physical properties. The adverse health properties of BTEX compounds are well documented.

Kao and Prosser (2001) suggested that accidental releases of petroleum products from underground storage tanks (USTs) are the most common cause of groundwater contamination. To put the problem into perspective, there are an

estimated 3 million USTs in the US containing petroleum-based products, 500,000 of which are believed to be leaking.

Other sources of groundwater contamination include the leaking or bursting of oil pipelines, operator mishandling (valves not opened/ closed properly) and spillages from road tankers. These are all examples of point source pollution. However, hydrocarbons can also enter the subsurface environment by diffuse sources i.e. atmospheric deposition and storm water run off.

The storage of fuel within the UK is covered by the Petroleum (Consolidation) Act 1928 (EA, 1999). The act requires that any storage of petroleum must be authorised by licence. Also included within the act is the loading of petroleum products from road tankers (at licensed premises).

The US, Europe and the UK have recently introduced regulations requiring the upgrading of underground storage tanks (USTs) to meet specific standards (Day *et al*, 2001). These new standards have been seen to significantly reduce the instances of fuel oil contamination of groundwater.

Nadim *et al* (2000) suggested that proper management of USTs, including the replacement of old and leaking USTs with new double wall tanks equipped with leak detectors and cathodic protection devices could significantly improve the quality of the groundwater source.

Although new leak detection devices fitted to USTs are capable of detecting leaks as low as 0.2L/h, they are unable to detect leaks below this rate. Some leaks may therefore go undetected for some period of time. Day *et al* (2001) suggested that these types of leaks can have the capacity to contaminate shallow groundwater systems, particularly if the subsurface environment did not readily support natural attenuation.

If an organisation within England intends storing 200 litres (45 gallons) of fuel/ oil (or more), then they will need to comply with the Control of Pollution (Oil Storage) (England) Regulations 2001 (Oil Storage Regulations). The regulations apply to industrial, commercial and institutional sites. Existing oil storage facilities in significant risk locations must comply with the regulations by 01/09/03, with all other existing locations requiring compliance by 01/09/05 (EA Pollution Prevention Guidelines PPG2). Similar regulations are due to be introduced in Scotland where the regulating body is SEPA. The EA is

responsible for the enforcement of the regulations, and in some cases can serve notices requiring facilities to be brought up to the required standard.

The EA Pollution Prevention Guidelines PPG2 provide guidance to those responsible for above ground oil storage tanks at sites other than oil refineries and distribution depots. EA guidelines also state that oil should not be stored within 10m of a watercourse or 50m from a well or borehole.

1.1.4. Drinking Water Regulations.

World-wide drinking water standards are becoming increasingly more stringent. For example in the UK during December 2003, new drinking water standards came into effect. Within the UK benzene is now the only hydrocarbon having a maximum permissible limit (1.0µg/L). However, elevated concentrations of other petroleum hydrocarbons may affect the organoleptic quality of the water.

The DWI provides data on UK drinking water regulations, for both industry and members of the public. The new 1998 EC Directive was introduced to replace the 1980 EC Directive. This was transposed into new UK regulations by 25/12/00 and came into force on 25/12/03, when the current regulations were replaced.

The old standard for the groups of substances relevant to this study found in the current Water Supply (Water Quality) Regulations 1989 (which implement the 1980 EC Directive on the Quality of Water intended for human consumption) were defined as follows:

- Dissolved or emulsified hydrocarbons (after extraction) with petroleum ether;
  mineral oils - 10 µg/l
- Substances extractable in chloroform - 1 mg/l dry residue.

Both these standards were deemed unsatisfactory, as they are both non-specific.

The new Directive and therefore the new regulations do not contain the above standards. Europe was persuaded that they were not useful for controlling drinking water quality. The new standard now contains:

- Benzene - 1.0 µg/l.

The US maximum contaminant level goal for benzene is zero (0µg/L). However, the maximum contaminant level for benzene in the US is 5.0µg/L (USEPA, 2003). Note that this is higher than the standards set in the UK.

There are no standards for MTBE or the remainder of the BTEX compounds within the UK. However, MTBE and BTEX compounds are readily detected in drinking water because at low concentrations they can impart a noticeable taste or smell. The organoleptic quality of the water (for example its taste or smell) is affected below concentrations that might pose a health risk to the consumer. Keller *et al* (2000) stated that the maximum contaminant level for MTBE was set as 5.0µg/L in the state of California.

1.1.5. Overview of BTEX and MTBE Compounds.

Kao and Prosser (2001) stated that BTEX compounds are major components of petroleum products, with gasoline containing the most. BTEX compounds have been found to impact on the groundwater environment. They also pose a major health risk. Compared to other compounds found in petroleum (for example aliphatic compounds), BTEX compounds are very soluble in water. This means that they are easily transferred to groundwater after pollution incidents. The compounds can be then transported downstream of the initial contamination.

Refer to section 1.3.2.2 for chemical and physical properties of BTEX compounds.

Sources of BTEX contamination of groundwater include accidental emissions from industrial effluents and atmospheric pollution. However the most common source of BTEX pollution of groundwater are spills involving the release of petroleum compounds such as gasoline, diesel fuel, lubricating and central heating oil from leaking tanks (Nollet, 2000).

Instances of BTEX contamination issues still continue today. The EA reports on such incidents and the information is easily accessed from their website. For example in 2002, Huntsman Petrochemicals (UK) Ltd was fined £23,000 after 100 tonnes of benzene escaped into the river Tees. A storage tank had not been closed correctly, causing the release of benzene. On this occasion, the EA deemed the environmental impact of the benzene to be low.

MTBE is the most commonly used ether-oxalate used within fuels. It replaces not only lead as the preferred anti knock agent, but also the known carcinogen benzene.

In the US there has been a requirement to improve air quality as part of the Clean Air Act (CAA), 1990. MTBE has been extensively used throughout the US to

improve fuel combustion and reduce vehicle emissions of a wide range of pollutants that affect air quality. Since the introduction of MTBE to reformulated gasoline in 1990, there is evidence to suggest the use of the compound has led to noticeable improvements to air quality throughout the United States (Rong, 2001).

Graham *et al* (2003) stated that currently, MTBE makes up approximately 11% (vol/vol) of 'oxy-fuels' and 15% (vol/vol) of reformulated gasoline, although this most likely relates to fuel sold in the US. However when added to UK unleaded gasoline, the MTBE concentration is typically less than 1%. Within premium unleaded and lead replacement fuel the level of MTBE in the UK can be up to 5%. However, use of these fuels is falling. The maximum legal use of MTBE within UK fuels is 15% by weight (EA, 1999).

Adam *et al* (2002) wrote that although the use of MTBE within UK fuels was currently low, this could change due to the new European Union (EU) directive on fuel quality and vehicle emissions. Also, the European gasoline quality requirements (which form part of the EC Directive 98/70/EC) include the requirement to reduce the overall aromatic content of the fuel. It was stated (EFOA, 2000) that because reducing the aromatic content of the fuel effectively reduces the octane rating of the fuel, that there would be an increasing need for compounds such as MTBE within European fuels.

Although the introduction of MTBE had been seen to significantly improve air quality, paradoxically there have been a large number of incidents (especially in the state of California) where MTBE has caused widespread groundwater pollution (Davis and Powers, 2000). Groundwater is extremely susceptible to contamination by MTBE because of the compound's chemical and physical properties (most notably its high solubility). This has also meant that the remediation of groundwater contaminated with MTBE is very costly.

MTBE represents a serious complication in the remediation of contaminated aquifers for a number of reasons;

1) MTBE is highly soluble and can travel long distances within aquifer systems.
2) MTBE degrades very slowly under aerobic conditions.
3) MTBE has not been observed degrading under anaerobic conditions.

A report by Dottridge and Hall (2000) suggested that MTBE and other ether oxygenates did not currently pose a major threat to groundwater supplies within England and Wales. This was because ether oxygenates are currently not found in significant concentrations within UK fuels. The report concluded that if the level remains the same the number of boreholes with tasteable concentrations of MTBE is thought unlikely to rise. Certainly there will not be problems like those seen in the US. However, if the concentration of MTBE within UK fuel increases to 5%, then this would most likely increase the incidents of taste related problems significantly. Whatever the fate of MTBE usage in UK fuels, it is clear that lessons must be learnt from the US model.

Ethanol can be used as a cheap alternative to MTBE. Along with MTBE it is used to reduce vehicle emissions of carbon monoxide and ozone precursors. Unlike most other fuel compounds and additives, ethanol is a renewable energy source. Brazil is the only country in the world so far to adopt ethanol as a viable alternative to non-renewable fuel source. It is used in gasoline and more recently in diesel (up to 3%). New legislation introduced in the US now supports the use of ethanol as the common oxygenate, whilst banning the use of MTBE (Adam et al, 2002). The environmental impact of ethanol is currently under investigation in order to avoid similar problems seen when there was a lack data relating to the contamination of groundwater with MTBE. A number of studies have been carried out on gasoline-ethanol fuels, but not diesel-ethanol fuels.

Refer to section 1.3.2.2 for a more detailed investigation of the chemical and physical properties of MTBE.

1.1.6. Toxicology of and Organoleptic Aspects of BTEX and MTBE Compounds.

The World Health Organisation (WHO) provides toxicology information on specific compounds including BTEX (WHO, 2003).

Benzene.

Acute exposure to high concentrations of benzene primarily affects the central nervous system. At lower concentrations, benzene is toxic to the haematopoietic system, thus causing haematological changes including leukaemia. The International Agency for Research on Cancer (IARC) has classified benzene in Group 1 (most hazardous).

Based on a risk estimate using data on leukaemia from both epidemiological and inhalation exposure, it was calculated that a drinking water concentration of 10μg/L was associated with an increased lifetime cancer risk of 10^{-5} (a probability of 0.00001).

As data on the carcinogenic risk to humans following ingestion of benzene are not available, risk estimates were based on a 2-year study of ingestion in rats and mice. The estimated range of benzene concentrations in drinking water corresponding to an excess lifetime cancer risk of 10^{-5} is 10–80 μg/litre. The lower end of this estimate corresponds to the estimate derived from epidemiological data, which formed the basis for the previous guideline value of 10μg/litre associated with a 10^{-5} excess lifetime cancer risk. WHO therefore retained the guideline value of 10 μg/litre for a 10^{-5} excess cancer risk.

Toluene.

Toluene has a low acute oral toxicity, and there is no evidence so far of any carcinogenic properties. The WHO guideline for toluene in drinking water is 700μg/L. However, this value exceeds the lowest reported odour threshold for toluene in water. Toluene has a sweet, pungent, benzene-like odour and the reported taste threshold ranges from 40 to 120 μg/litre (WHO, 2003).

Ethylbenzene.

Ethylbenzene has a low acute oral toxicity. There is no data on reproduction, long-term toxicity, or carcinogenicity with respect to ethylbenzene. The WHO

guideline for ethylbenzene in drinking water is 300µg/L. Ethylbenzene has an aromatic odour and the taste threshold ranges from 72 to 200 µg/litre. Note that the lowest odour threshold is lower than the health-based guideline value derived for the compound.

Xylenes (M-P-O).

The acute oral toxicity of xylene isomers is low. The WHO guideline for xylene isomers in drinking water is 500µg/L. The odour threshold for xylene isomers in water has been reported to range from 20 to 1800 µg/litre. Note that the lowest odour threshold is lower than the health-based guideline value derived for the compound.

MTBE.

Past toxicological data for MTBE suggests that it is of low toxicity and does not appear to be carcinogenic. However, the US government has recently labelled the compound a potential carcinogen. Based on current toxicological data, Hartley *et al* (1999) suggested a maximum drinking water limit of 100µg/L. There are no current WHO guidelines for MTBE.

However, as previously stated, MTBE has a very low taste threshold and characteristic turpentine odour, typically ranging from 5 - 15µg/L.

1.1.7. Case Studies.

Anglian Water provided the data for case studies 1-2. The case studies investigated in this section highlight the points raised in section 1.1.3 and 1.1.5, in particular the problem related to BTEX and MTBE compounds. Other relevant case studies are included within the literature review.

1.1.7.1. Case Study 1: Isleham Water Treatment Works (WTW).

In July 1993 elevated concentrations of MTBE were recorded in 3 boreholes at Isleham WTW. Table 1.1 details the concentration of MTBE at the 3 boreholes of interest. Elevated concentrations of benzene, toluene and xylene (BTX) compounds were also found. An investigation by Anglian Water concluded that the high concentrations of MTBE had been due to an on site spillage of a quantity of gasoline. Note that the figures presented in the table were provided by

Anglian Water and that the detection limit of the analytical instrument used to quantify MTBE was not known.

Borehole	MTBE (μg/L)
4	32
2	0.1
3	2.8

Table 1.1 Elevated MTBE Concentrations at Isleham WTW.

An in-situ remediation method was employed to clean up the spillage. This included the physical removal of contaminated soil and the pumping of the contaminated groundwater. Pumping of the groundwater from within the boreholes can be carried out using borehole pumps. If an effective remediation method had been close to hand, then the borehole may not have had to be switched off for the duration of the pollution incident.

Table 1.2 illustrates the reduction over time in concentrations of MTBE and BTX compounds (in μg/L). The reduction was attributed to the in-situ remediation methods employed.

BOREHOLE	MTBE	BENZENE	TOLUENE	XYLENE
6 (2/9/93)	3425	5475	13440	9613
6 (4/1/94)	903	893	500	4498
7 (2/9/93)	1547	1761	4521	6735
7 (4/1/94)	770	1761	317	4058

Table 1.2. Reduction in MTBE/ BTEX Compounds seen at Isleham WTW after Remediation.

1.1.7.2. Case Study 2: Beck Row (Mildenhall).

Problems at Beck Row have been observed by various organisations for the past 20 years. Contamination events have included;

- A spillage of JP4 aviation fuel at the adjacent Mildenhall Airbase (Summer, 1978)
- A spillage of fuel from a gasoline station to the east of the site.

- The catch water drains to the northwest. The drain was contaminated with chlorinated ethylene's from the airbase surface water.

The problem of contamination at Beck Row still remains. In 1993 the National Rivers Authority (NRA), which is now the EA, reported a possible 86,000L diesel spillage from the airbase. Between 13/11/90 and 21/10/92, 10 boreholes were routinely sampled for BTEX and MTBE. A number of chlorinated hydrocarbons were also tested. BTEX compounds were tested a total of 411 times each, most recently on 04/05/99.

Benzene was found to be above the detection limit of 0.2 µg/L on 26 occasions. A maximum concentration of 4.7µg/L was found on 21/08/90. However, a more recent analysis (29/01/97) revealed a concentration of 3µg/L. Toluene was found above the detection limit (0.2µg/L) on 31 occasions, with a maximum of 0.7µg/L on 26/06/90. MTBE was sampled 450 times, most recently on 04/05/90. 53 samples were above the detection limit (0.1µg/L), with a maximum of 25.5µg/L. Throughout the contamination incident most hydrocarbons were found to be above detection limits, with maximums of 234µg/L for benzene, 970 µg/L for toluene and 419 µg/L for MTBE.

1.2. Groundwater and Geochemistry.

The aim of the Groundwater and Geochemistry section of the literature review is to introduce the science related to the subsurface environment. Related geological principles will be looked at, along with its associated geochemistry and microbiology.

The aim of this study was to concentrate on petroleum hydrocarbons once they have reached public water supply boreholes, rather than the behaviour of hydrocarbons in the subsurface environment. Hence only basic principles will be reviewed here.

1.2.1 Groundwater Movement.

The movement of water throughout the Earth's crust forms part of the hydrological cycle. Once precipitation has occurred, water passes through the surface of the ground in a process called *infiltration.* The movement of the water through the unsaturated zone towards the saturated zone is termed *percolation.* Finally, the movement of the water towards rivers, lakes and the sea is termed *groundwater flow* (Blyth, 1984).

The behaviour of groundwater systems is generally controlled by the porosity and permeability of the rocks in the immediate area (Drever, 1997). *Porosity* is defined as the ratio of the volume of the voids in the rock to the total volume of the rock. Sometimes this is expressed as a percentage. If there are few small voids within the rock, then the amount of water that can be held within the rocks will be small. *Permeability* relates to the number and size of the pores within the rock and the degree to which the pores are interconnected. *Permeable* rocks easily allow the passage of water, whereas *impermeable* rocks retard the passage of water. It can be noted that a rock can be both porous but relatively impermeable, allowing the passage of only a small amount of water. Rocks with a low porosity but possessing a few large cracks will allow the passage of water, but will not make an effective store of water. Layers of rock that effectively allow both the storage and passage of water throughout them are called *aquifers* (Price, 1987). Aquifers with high total porosity but with low effective porosity will remain troublesome in treating any contaminant (USEPA MTBE Fact Sheet#2, 1998).

Clays and shales (which are both relatively impermeable) or indeed any other impermeable media can occur at the surface and hence restrict the movement of water downwards. Also, if any impermeable media is present below an aquifer, this can restrict the movement of water downwards from the aquifer. An aquifer overlaid by an impermeable medium is termed a confined aquifer, whereas an aquifer overlaid by a permeable medium is termed an unconfined aquifer (refer to figure 1.3).

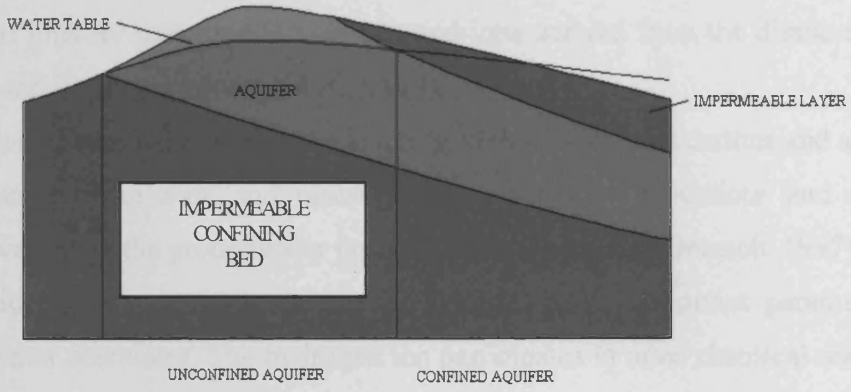


Figure 1.3. Representation of an Unconfined and Confined Aquifer. Source: Drever, 1997.

If sufficient pressure (or head) is available to force groundwater through the spaces between porous aquifer materials, then it will flow. The rate of movement is determined by the hydraulic gradient, permeability, and porosity of the material lying within the immediate area. The hydraulic gradient determines how quickly the groundwater moves from one point to another.

1.2.2. Groundwater Chemistry.

The chemical quality of a groundwater is a result of the combination of physical, chemical and microbiological processes (Alley, 1993).

The interaction between the organic contamination and the subsurface environment is an extremely important consideration when trying to predict the extent to which a contamination affects a particular groundwater system.

Water is an extremely polar solvent, and when organic pollutants come into contact with the water, they dissolve over time and are transported through the aqueous environment. The composition of a particular groundwater is dependent on the rock or soil with which it resides. Groundwater will contain numerous dissolved ions for example; H^+ , OH^- , and ions derived from the dissolution of organic and inorganic matter (Blyth, 1984).

Groundwater types are classified according to their dominant cations and anions. For example if calcium and bicarbonate were the major cations and anions respectively then the groundwater type would be Ca-HCO_3 (Deutsch, 1997).

The concentration of the hydrogen ion (or pH) is an important parameter in groundwater chemistry. The hydrogen ion participates in most chemical reactions that can affect the composition of groundwater, for example;

- Mineral dissolution/ precipitation: $CaCO_{3(aq)} + H^+ \leftrightarrow Ca^+_{(s)} + HCO_3^-$
- Aqueous hydrolysis: $Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$
- Adsorption/ desorption: $FeOH + Cu^+ \leftrightarrow FeOCu + H^+$

(eqn 1.1)

The pH of a water does not give an indication of the capacity of the system to maintain that pH, if an acid or base is added. Dominant inorganic carbon species usually act as buffering species, as they can both take up or release H^+ ions as part of their reactions.

For example on the addition of acids;

- $HCO_3^- + H^+ \leftrightarrow H_2CO_3$
- $CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$ **(eqn 1.2)**

Or on the addition of bases;

- $H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O$
- $HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$ **(eqn 1.3)**

Alkalinity can be described as the total acid-neutralising capacity of water (ANC), whereas acidity can be defined as the total base- neutralising capacity of water (BNC). Alkalinity is usually determined by titration with sulphuric acid (to an end point of pH4.5), whereas acidity is determined by titration with caustic soda (to an end point of pH8.3). The alkalinity of a groundwater is commonly determined, as it is dependent on the concentration of inorganic species within the system. This means that it can be used to quantify the amount of bicarbonate and carbonate. It can be noted that bicarbonate is often the dominant anion in shallow groundwaters.

Oxidation and reduction processes involve the transfer of electrons from one element to another, hence changing the valency of the element. In an oxidation reaction elements lose electrons, whilst in a reduction reaction, elements gain electrons from other species. The redox potential (Eh) is another important variable when investigating the geochemistry of a groundwater. The value of Eh is a measure of the tendency for the redox reaction to occur. The more positive the Eh the more likely reduction is to occur. The less positive, or more negative the Eh, the more likely oxidation is to occur (Freemantle, 1995). The solubilities of minerals formed from reduced or oxidised elements are dependent on Eh, and hence the value directly affects the mobility of these species within the aquifer.

Table 1.3 illustrates the redox potential of some important groundwater species.

← Oxidation HALF-REACTION Reduction →			
Oxidised Species	$+ ze^-$	Reduced Species	Eh/V
$Ca\ 2^+$ (aq)	$+2e^-$	Ca (s)	-2.87
$Mg\ 2^+$ (aq)	$+2e^-$	Mg (s)	-2.38
$Al\ 3^+$ (aq)	$+3e^-$	Al (s)	-1.66
$Pb\ 2^+$ (aq)	$+2e^-$	Pb (s)	-0.13
$2H^+$ (aq)	$+2e^-$	H_2 (g)	0.00
$Fe\ 2^+$ (aq)	$+2e^-$	Fe (s)	+0.77

Table 1.3. Redox Potential of Important Groundwater Species. Source: Freemantle, 1995.

As the Eh increases (becomes more positive), there is a tendancy for the forward reaction (reduction). As the Eh decreases (becomes more negative), there is a tendency for the reverse reaction (oxidation) to occur.
Section 1.3.4 of the literature review describes the influence of groundwater chemistry after fuel spillage.

1.2.3. Subsurface Microorganisms.

The degradation of organic components, which may have been transferred to a groundwater system, is mainly due to microbial processes (biodegradation). Biodegradation occurs when waste materials are metabolised by microorganisms within the subsurface environment. Microorganisms sustain life by continuously cycling organic and inorganic substances (Alley, 1993).
For degradation to occur, the correct condition must be met (Coduto, 1999). These include;

1) The presence of carbon based materials – for example petroleum hydrocarbons.
2) The correct organisms. The organisms can occur naturally or can be introduced as part of a remediation program.
3) Terminal electron acceptors (for example O_2 and CO_2).
4) Other nutrients such as calcium, nitrogen and phosphorus.
5) The environmental conditions must be correct. These include temperature, pH and salinity.

It is widely accepted that petroleum hydrocarbons can be degraded by a number of different microbial conditions. These include; aerobic and anaerobic-oxidising conditions, nitrate-reducing, Fe(III)-reducing, sulphate-reducing and methanogenic conditions (Chapelle, 2001).
The activity of microorganisms can give important information concerning the overall fate and transport of organic particles. This is because compounds are degraded in different ways (or not at all), and will depend upon the groundwater system it resides. The substrates, intermediate products and final products of the microbial transformations are usually water soluble, and hence can be transported by groundwater.

Previously considered inert compounds such as MTBE, are now known to be degradable under certain conditions (Chapelle, 2001). A study conducted by the USEPA (2000) looked at the natural attenuation of MTBE in the subsurface under methanogenic conditions. The study was conducted at a former fuel oil plant in Elizabeth City, North Carolina, US. Laboratory experiments were conducted to find the extent of the biodegradation of MTBE. There was both extensive removal of MTBE from laboratory microcosms that were supplemented with alkylbenzenes, and extensive removal when alkylbenzenes were not present. In both experiments however there was an extensive lag period of approximately 175 days when MTBE had not been observed degrading. BTEX compounds were removed from the microcosms all within 175 days. The removal of MTBE within the microcosms did not require the presence of BTEX compounds, however the removal of MTBE did not begin until the biodegradation of BTEX compounds was complete.

A first order rate of removal of MTBE was observed in the study and was found to be a sensitive function of ground water seepage velocity. First order biodegradation is expected when the chemical concentration is below the substrate concentration and the organisms are not increasing in abundance. This could be because there is not sufficient carbon to support a doubling, possibly because some other limiting nutrient is lacking (Alexander, 1994). Tertiary Butyl Alcohol (TBA) is a known transformation product of MTBE. TBA was found in some areas of the contamination plume, this corresponded to a reduction of MTBE. The presence of TBA in this instance suggested that it had been produced as a transformation product.

1.3. Petrochemicals.

The aim of the petrochemical section of the literature review is to introduce relevant chemistry related to petrochemical hydrocarbons. The section includes; hydrocarbon chemistry, crude oil and fractional distillation and the chemical constituents of fuels. Particular emphasis is given to BTEX and MTBE compounds.

The behaviour of petrochemicals in the subsurface environment is also discussed.

1.3.1. Crude Oil and Fractional Distillation.

Crude oil consists of a mixture of hydrocarbons of varying molecular weight. The number of carbon atoms in the compounds found in crude oil range from 1 (methane) to 400 (Chapelle, 2001). With respect to individual atoms - the average crude oil contains; 84.5% carbon, 13% hydrogen, 1.5% sulphur, 0.5% nitrogen and 0.5% oxygen. With respect to classes of compounds (for example those illustrated in section 1.3.2), a typical crude oil might contain; 25% alkanes, 50% cycloalkanes, 17% aromatics (including polyaromatic hydrocarbons -PAHs) and 8% asphaltics (Fetter, 1993). Asphaltics are molecules of very high molecular weight with more than 40 carbon atoms.

Crude oil differs vastly in its organic constituents depending upon where it was found. For example; Pennsylvanian crude consists of 90-95% *n*-alkanes, whilst crude oil found in Western Mexico contains just 50% *n*-alkanes. The relative worldwide uniformity of individual petroleum products such as gasoline is due to refining technology rather that the origin of the crude oil (Chapelle, 2001).

Refineries use a procedure called 'cracking' to fractionate the fuel into useable cuts (Nadim *et al*, 2000). This process involved heating crude oil to a temperature of 230°C, with or without the presence of catalysts. This procedure breaks down the complex/ heavy molecules of the crude oil into simpler/ smaller molecules. It is from these simpler molecules that different fuels are blended.

The differing constituents of petroleum represent progressive cuts on a distillation column. These depend upon the boiling point of the constituents (hence dependent on the number of carbon atoms present). Table 1.4 illustrates cuts of petroleum on a distillation column.

Fraction	Range of Carbon atoms per molecule	Boiling point range (°C)	Uses
Gas	1 – 4	20	Cooking/ Heating
Gasoline	5 – 10	20 – 190	Fuel
Kerosene	11 – 13	190 – 260	Fuel, Jet Fuel
Diesel	14 – 18	260 – 360	Diesel Fuel and Fuel Oil
Heavy gas/ lubricating oils	19 – 40	360 – 530	Lubricating Oil, Greases, Waxes
Residuum	> 40	> 560	Asphalt

Table 1.4. Crude Oil Cuts. Source: Fetter, 1993.

1.3.2. Petroleum Compounds.

Petroleum compounds contain a wide range of hydrocarbons; from butane to decane and benzene to naphthalene, and cover boiling points in the range of 50°C-281°C.

Hydrocarbons (like those found in petrochemicals) are classified by the number of carbon atoms present, how the carbon atoms are bonded to each other, and the presence and number of functional groups. Listed below are some important petrochemical hydrocarbons.

1.3.2.1. Aliphatic hydrocarbons.

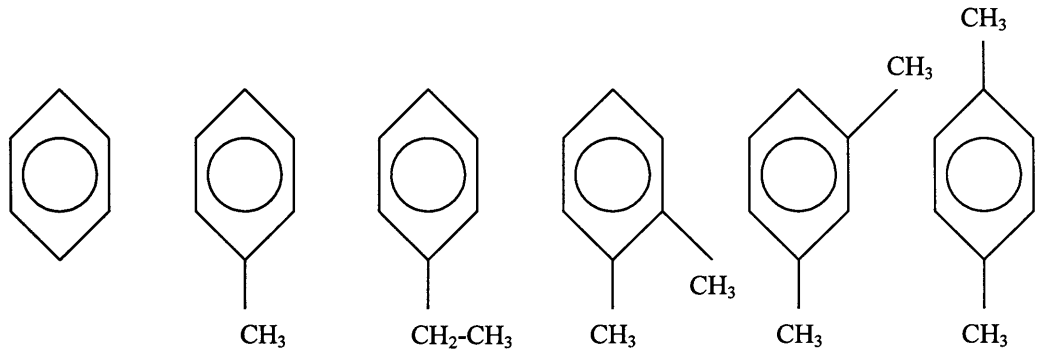
Aliphatic compounds are found in petroleum and are compounds with more than one carbon atom. They can be joined by single bonds (alkanes – sometimes termed paraffins), double bonds (alkenes – sometimes termed olefins), or triple bonds (alkynes).

Nyer and Skladany (1989) stated that the number of carbons in the compound changes the properties of the chemical dramatically. Alkane chains with C_5-C_{17} are liquids at room temperature and have densities less than that of water (<1 g/cm^3). Alkanes with C >18 are solids at room temperature (usually waxes). Alkane solubility in water rapidly decreases as the number of carbons in the compound increase. The vapour pressure of a compound decreases as the number of carbons increase (the higher the vapour pressure, the greater the volatility).

The boiling point of a hydrocarbon compound increases with the number of carbons. **Cycloalkanes** have similar chemistry to that of straight chain alkanes.

1.3.2.2. Aromatic hydrocarbons.

Aromatic hydrocarbons are found in different quantities within fuels and are generally more soluble and volatile than aliphatic compounds. Aromatic compounds are based on the benzene ring. Benzene contains six carbon atoms bonded together to form a hexagon shape. The structure is held together by particularly stable bonds containing delocalised clouds of pi-electrons, making the compound very stable. Cyclohexane on the other hand is less stable as the carbon atoms forming the ring are formed of single bonds. Toluene, Ethylbenzene and Xylene isomers (TEX) are important aromatic compounds. TEX compounds are formed of benzene, with the addition of methyl functional groups. Figure 1.4 illustrates the structure of these BTEX compounds



1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = *ortho*-xylene, 5 = *meta*-xylene and 6 = *para*-xylene.

Figure 1.4. Structure of BTEX Compounds.

Table 1.5 details important physical properties of BTEX compounds, stated at 20-25°C.

	Molecular Weight	Solubility (mg/L)	Boiling Point (°C)	Melting Point (°C)	Vapour Pressure (mm Hg)	Unitless Henry's Law Const.
Benzene	78	1750	80	5.5	95	0.22
Toluene	92	515	111	-95	30	0.26
Ethylbenzene	106	152	136	-94.4	10	0.32
M-xylene	106	158	139	-47	8	0.22
P-xylene	106	156	139	13.2	7	0.22
O-xylene	106	175	144	-25	7	0.22

Table 1.5. Physical Properties of BTEX Compounds. Source; Perry and Green, 1984.

1.3.2.3. MTBE and other Performance-Enhancing Ether Oxygenates.

Ether oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl butyl ether (TAME) were developed to enhance the performance of unleaded, super unleaded and lead replacement fuels (LRF). Ether oxygenates also reduce the amount of unburnt hydrocarbons that are released into the atmosphere. Non-ether oxalate performance-enhancing additives include methanol. Figure 1.5 details the chemical structure of MTBE, ETBE and TAME.

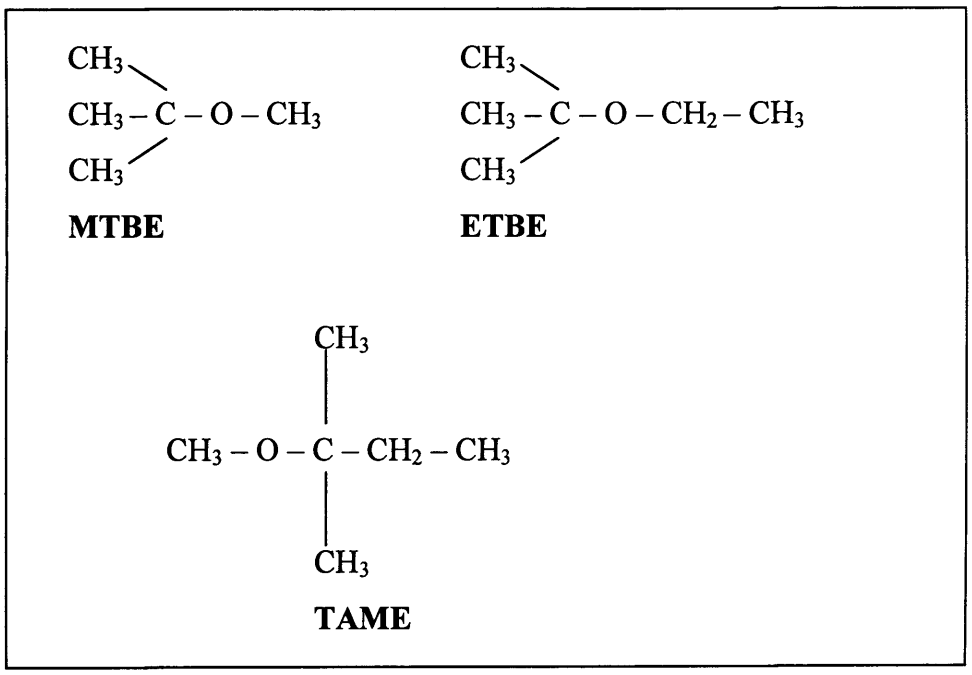


Figure 1.5. Chemical Structure of MTBE, ETBE and TAME. Source: EA, 1999.

Tables 1.6 and 1.7 detail physical properties of MTBE and ETBE/ TAME respectively.

PARAMETER	VALUE
Common Names	MTBE (Methyl Tertiary Butyl Ether) TBME (Tertiary Butyl Methyl Ether) 2-Methoxy-2methylpropane.
Physical State	Liquid
Colour	Colourless
Odour threshold	680 ppb
Taste threshold	2-3 ppb
Water Solubility	48g/100g at 20°C
Co-solubility effect	None
Density	0.7404g ml^{-1} at 20°C
Vapour Pressure	32.66kPa at 25°C
Aqueous Half Life	540 min
Dimensionless Henry's Law Constant	0.018 @ 20°C
Molecular Weight	88.15
Melting Point	-110°C
Boiling point	55°C
Log partition coefficient	
Octanol/water (K_{ow})	0.94 – 1.30
Fuel/water (K_{fw})	1.55 at 22°C
Drinking water Standards	EEC, WHO, EA - None

Table 1.6. Physical Properties of MTBE. Source: Burgess *et al,* 1998.

Property	ETBE	TAME	Unit
Structural Formula	$C_6H_{14}O$	$C_6H_{14}O$	-
Density (20°C)	740	740	kg m^{-3}
Aqueous Solubility(20°C)	26,000	20,000	mg l^{-1}
Solubility in gasoline	Miscible	Miscible	-
Log K_{oc}	1.0-2.2	1.3-2.2	-
Dimensionless Henry's Law Const.	0.11	0.052	-
Odour Threshold	49	194	µg l^{-1}
Taste Threshold	47	128	µg l^{-1}

Table 1.7. Physical Properties of ETBA and TAME. Source: Burgess *et al,* 1998.

1.3.2.4. Polycyclic aromatic hydrocarbons (PAHs).

PAHs are formed when two or more benzene rings are joined together. The simplest PAH is naphthalene (Fetter, 1993). Naphthalene consists of two benzene rings. PAHs are found in heavy fractions of petroleum distillation. Figure 1.6 illustrates the structure of Napthalene. Napthalene is a major soluble (aromatic) fraction of Diesel.

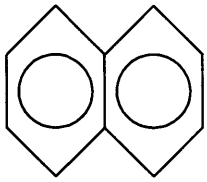


Figure 1.6. Structure of Napthalene.

1.3.3. Fuel Types.

When characterising a fuel after a spillage it is important to recognise the variability of the mixture. This is caused by different fuel manufacturers/ brands, geographical source, season and daily refinery operations (Thomas and Delfino, 1991). The composition of the fuels presented in this chapter is therefore very subjective. Knowledge of the compositional breakdown of a fuel involved in a contamination event must be a priority for the remediation effort.

Kaplan *et al* (1996) studied the alteration of hydrocarbon fuels in the environment and as part of the work analysed a number of different fuels. Table 1.8 denotes the percentage concentration of a number of hydrocarbon groups found in gasoline, diesel and central heating oil (kerosene).

Composition	Gasoline	Diesel	Central Heating Oil.
Paraffins	45	55	14
Cycloparaffins	5	12	7
Olefins	7	5	-
Aromatics	43	24	34
Polar + Residuals		4	45

Table 1.8. Compositional Data of Typical Hydrocarbons found different Fuels (%). Source: Kaplan *et al,* 1996.

1.3.3.1. Gasoline.

Gasoline (or petrol) is a term used to describe volatile, inflammable petroleum fuels often used in the internal combustion engine. It is in general a mixture of petroleum chemicals with boiling points less than that of decane (36-173°C) (Nyer and Skladany, 1989). There are more than 300 recognised individual compounds in gasoline, although only about 90 major hydrocarbons are routinely analysed.

Hartley and Englande Jr (1992) quantified the different constituents of gasoline as having approximately 56% alkanes, 34% aromatics, 10% alkenes and <1% polynuclear aromatic hydrocarbons.

Kaplan *et al* (1996) quantified the common range of compounds within gasoline as being from propane (C_3) to dodecane (C_{12}). These are examples of low molecular weight alkanes. C_{13} and C_{14} n-alkanes are sometimes detected - often when the fuel has been altered by evaporation.

Gasoline has a high aromatic composition, and contains a relatively large concentration of BTEX compounds. The mixture has very little polyaromatic hydrocarbons (PAHs).

BTEX compounds can represent approximately 18% (w/w) of a standard gasoline formulation, with benzene (recognised as the most toxic compound) forming approximately 11% of the BTEX fraction. Toluene represents 26%, ethylbenzene 11% and the xylene isomers 52%.

A recent full component breakdown of unleaded gasoline (95 Octane) and super unleaded gasoline (97 Octane) can be found in the Appendix A. Super unleaded fuels require larger concentrations of branched alkanes, aromatic hydrocarbons and fuel oxygenates. Lead replacement fuel (LRF) has the same basic composition of super unleaded fuels, with the addition of a potassium-based additive.

MTBE is added to gasoline in varying amounts. Information regarding MTBE can be found in section 1.1.5.

1.3.3.2. Diesel.

Diesel and jet fuel vary from gasoline in that they consist primarily of higher boiling point straight chain alkanes (Nyer and Skladany, 1989 and Chapelle, 2000). Diesel is characterised on a mass chromatogram by showing a smooth n-

alkane distribution pattern, maximising at C_{14} to C_{17} and diminishing at about C_{23}. It also has an isoparaffin distribution pattern from I-C_{10} to I-C_{20}(phytane), with I-C_{19}(pristane) the dominating compound (Kaplan *et al,* 1996). Figure 1.7 shows a typical diesel chromatogram.

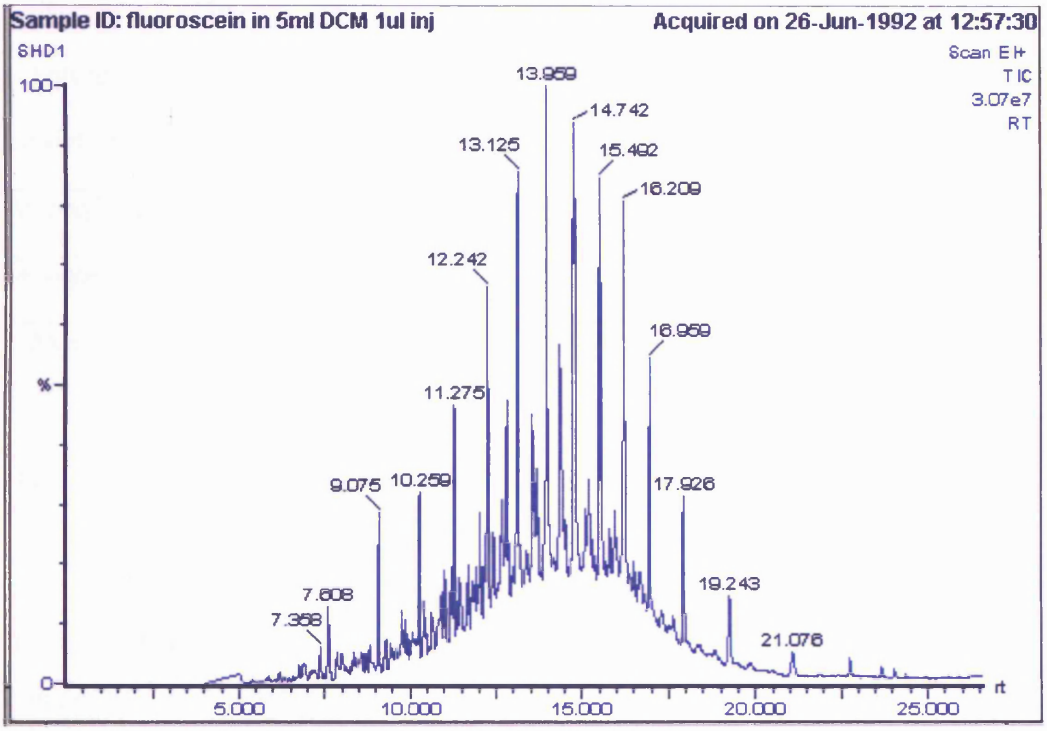


Figure 1.7. Diesel Chromatogram. Chromatogram obtained at UCL within Wolfsen Geological Laboratory.

Diesel does not have the quantity of BTEX compounds that is added to gasoline. However BTEX compounds are found in detectable concentrations in diesel and kerosene fuels.

To illustrate this, Table 1.9 denotes concentrations of BTEX compounds found in water after contact with diesel, kerosene and gasoline and fuel oil samples. Data was taken from 2 sources; Thomas and Delfino, 1991 and Chapelle, 2001. Differences in average concentration of the compounds can be attributed to differences in the diesel fuels analysed.

	Average Concentration of BTEX Compounds (µg/L)							
	Diesel		Kerosene		Gasoline		Fuel Oil	
Data Source	Thomas	Chapelle	Thomas	Chapelle	Thomas	Chapelle	Thomas	Chapelle
Benzene	18	344	24	294	130	N/A	N/A	203
Toluene	36	777	88	870	978	N/A	N/A	509
Ethylbenzene	46	139	28	19	75	N/A	N/A	100
M/P-xylene	20		58		311	N/A	N/A	
O-xylene	20		36		144	N/A	N/A	
Xylenes		875		1260		N/A	N/A	592

Table 1.9. Average Concentration of BTEX Compounds found in Various Fuels. Source: Thomas and Delfino, 1991 and Chapelle, 2001.

Although MTBE is not intentionally added to any fuel other than gasoline, the compound has been found in detectable concentrations within fuels other than gasoline. Robins *et al* (1999) suggested that MTBE had been found in central heating fuel oil whilst Robins *et al* (2000) suggested that MTBE had been found in diesel. The levels of MTBE found by Robins *et al* (2000) both in fuel oil (9.7 – 906mg/L) and diesel (74 – 120mg/L) were considered to be large enough to significantly pollute a groundwater source. The full extent to the level of MTBE within fuels other than gasoline and its source are not yet known.

1.3.4. Hydrocarbon Chemistry in the Subsurface Environment.

This sections details the influence of the physical properties of hydrocarbons, and how they interact in the subsurface environment.

1.3.4.1. Physical Properties of Hydrocarbons.

A number of physical properties of hydrocarbons must be considered when attempting to predict how the substance will behave in the aquatic subsurface environment (Fetter, 1993). These include;

Specific Gravity. The ratio of the weight of a given volume of substance (solid or liquid) to the weight of the same volume of water.

Water Solubility. For a liquid this is a function of the temperature of the water and the nature of the substance. For a gas water solubility is measured at a given vapour pressure. Organic species can have solubilities ranging from completely miscible with water, to almost insoluble. Soluble substances will have a greater mobility in the aquatic subsurface environment.

Octanol-water partition coefficient (K_{OW}). The coefficient is a measure to which an organic species will preferentially dissolve in either water or an organic solvent. The coefficient is measured by adding the substance to equal amounts of water and octanol, where the ratio of the equilibrium concentration of the substance in both the octanol and water is expressed as a logarithm. The greater the logarithmic value, the greater the tendency to dissolve in the organic liquid rather than in water, hence the less mobile the compound will be in the environment.

Vapour Pressure. This is the measure of the tendency of a substance to pass from a solid or a liquid to a vapour state. It can be defined as the pressure of the gas, in equilibrium with the liquid (or solid) at a given temperature. The greater the vapour pressure the more volatile the compound.

Henry's Law Constant. The most common definition of Henry's Law states that the amount of gas dissolved in a given quantity of liquid (at constant temperature and total pressure) is directly proportional to the partial pressure of the gas above the solution.

The equation for Henry's Law based upon the above definition is;

$$H_{p/c} = P_x/C_x \qquad \textbf{(eqn 1.4)}$$

Where P_x = partial pressure of gas (atms at given temperature), C_x = equilibrium concentration of the gas in solution (mol/m^3 water) and $H_{p/c}$ = Henry's Law constant in atm/(mol/m^3 water). Henry's Law can be considered as the partition coefficient that describes the tendency for a compound to separate (or partition), between the gas and the liquid at equilibrium (Dyksen and Hess, 1982).

The Henry's Law Constant for specific compounds can also be expressed in different forms or units. Table 1.10 details the different expressions of Henry's Law Constant.

	Theoretical Basis of Henry's Law Constant	Units
$H_{P/C}$	Partial pressure of gas/ equilibrium concentration of gas in solution	atm m^3/ mol
$H_{C/C}$	Concentration of substance in gas/ concentration of substance in solution	Dimensionless
$H_{MF/MF}$	Mole fraction Y in gas/ mole fraction X in solution	Dimensionless
$H_{P/MF}$	Partial pressure of gas/ mole fraction X in solution	Atmospheres

Table 1.10. Different Expressions of Henry's Law Constant.

$H_{C/C}$ and $H_{MF/MF}$ are expressed in dimensionless form because they represent either ratios of concentrations or ratios of mass fractions. The values of Henry's Law Constants can differ greatly and if required can be converted between forms. Henry's Law Constants are temperature and pressure dependent.

Note that unless otherwise stated, the Henry's Law Constants applied in later sections of this study are expressed in dimensionless form (specifically $H_{C/C}$) and is referred to from this point onwards as H. The greater the Henry's Law constant (H), the greater the driving force for transfer of the solute from solution to the gaseous phase (Roberts *et al,* 1982). In particular the dimensionless Henry's Law Constant is applied to air-stripping design theory in section 1.6.1.3 and hence the amenability of specific compounds to remediation techniques.

1.3.4.2. Aqueous Solubility of Petroleum Compounds.

An important parameter when dealing with the fuel oil contamination of groundwater is the solubility of the organic compound.

Solubility can be considered the equilibrium concentration of a compound dissolved in water, when the water is in contact with the pure compound only. The greater the solubility, the greater the concentration of the compound in water.

Water is a polar compound and petroleum compounds are generally non-polar. Petroleum compounds hence are not considered to be particularly soluble in water. However, aromatic compounds including BTEX compounds are considered to be relatively soluble in water (Drever, 1997). The solubility of hydrocarbons greatly increase with the addition of an oxygen atom (for example MTBE).

The maximum concentration of a pure compound-water mixture equals the compound's solubility. Within a mixture, the concentration of each compound within the water is equal to its mole fraction in the mixture multiplied by its specific solubility:

The solubility of a specific compound within a mixture is less than that within a pure compound-water mixture. Table 1.11 shows the aqueous solubility BTEX compounds in their pure-phase (in water) and the solubility of BTEX within a gasoline-water mixture (Nadim *et al*, 2000).

	Solubility of Pure Phase BTEX in Water (mg/L)	Solubility of BTEX in Gasoline-Water Mixture (mg/L)
Benzene	1791	51.4
Toluene	534.8	29.2
Ethylbenzene	140	3.8
o-xylene	175	6.2
m-xylene	146	9.2
p-xylene	156	3.4

Table 1.11. Pure Phase Solubility of BTEX Compounds in Water and Solubility of BTEX in Gasoline-Water Mixture. Source: Nadim *et al*, 2000.

1.3.4.3. The Effect of Cosolvency on the Solubility of Hydrocarbons in Water.

The solubilities of most pure hydrocarbons are known. However Poulsen *et al* (1992) observed that some fuel additives such as the octane-enhancing oxylate compound methanol can increase the solubility of specific fuel hydrocarbons. Poulsen *et al* (1992) suggested that the solubility of BTEX compounds was

greater when using a fuel high in methanol and a high fuel-to-water ratio. In contrast, Poulsen *et al* (1992) found that a fuel containing 15% MTBE was unlikely to produce enhanced BTEX concentrations in groundwater.

As a result of cosolvency, the release of high-methanol fuels into the groundwater could have a more serious effect than the release of methanol-free fuels. High concentrations of BTEX and methanol are likely to be found at the leading edge of a groundwater plume.

Groves *et al* (1998) also studied the effect of cosolvency for a number of gasoline range hydrocarbons. The aqueous solubility of benzene and *n*-hexane in the presence of methanol, ethanol and MTBE was investigated specifically. Groves *et al* (1998) and Cline *et al* (1991) found that MTBE did not affect hydrocarbon solubility in the aqueous phase. For the hexane-methanol, hexane-ethanol, benzene-ethanol and benzene-methanol systems, the cosolvents (which are completely miscible in water) caused a considerable increase in hydrocarbon solubility.

The presence of solubility-enhancing compounds within fuels must be considered when predicting the extent to which a fuel spillage might affect groundwater.

1.3.5. Behaviour of Fuel Oils in the Subsurface Environment.

1.3.5.1. Transport of Fuel Oils to the Aquifer.

Petroleum hydrocarbons can be released into the subsurface environment in a number of ways. These include the leaking of USTs, the continued leaking or bursting of oil pipelines, and also through accidental spillages (for example road tankers). These are examples of point sources of pollution, however hydrocarbons can also enter the subsurface environment by diffuse sources i.e. atmospheric deposition and storm water run off.

The movement of petrochemical hydrocarbons within soil and groundwater is controlled by a number of site-specific conditions (EA, 1999). Conditions include; the quantity and duration of the release, soil type, depth to water table, redox potential, pH, oxygen concentration, the potential for biodegradation, temperature and rainfall.

Day *et al* (2001) suggested the fate and transport of specific fuel compounds within the subsurface environment would be determined by a combination of

their physical and chemical characteristics, and also by the hydrogeological and geochemical conditions of the site.

Once a petroleum contamination has occurred, fuel will partition into three phases; the dissolved phase, the liquid phase and the gaseous phases (Nadim *et al*, 2000). A fraction of the mixture will dissolve into the soil moisture and groundwater, a liquid fraction will remain in the soil voids in its pure form (otherwise known as non-aqueous phase liquids or NAPLs), and a gaseous fraction will occupy the air spaces within the soil pores.

NAPLs are pure phase liquids which do not readily dissolve in water. They can be subdivided into two classes:

- Light non-aqueous phase liquids (LNAPLs). These compounds are lighter than water. Examples of LNAPLs fuels are gasoline, heating fuel, kerosene and aviation fuel.
- Dense non-aqueous phase liquids (DNAPLs). These compounds are heavier than water.

When a fuel oil contamination has occurred, the compounds will migrate downwards under the influence of gravity (with some lateral spreading). Lateral spreading can be caused by less permeable substances such as clays and shales, and will depend upon the local geological conditions. Once released, low molecular weight volatile petroleum compounds with the highest vapour pressure held within the air voids will escape rapidly. As petroleum compounds are NAPLs, a pool of NAPLs will form on the surface of the water table (Nadim *et* al, 2000). The soluble components of the fuel in contact with the water table will slowly dissolve and form a contamination plume moving downstream of the contaminated area. The soluble fractions of NAPLs include BTEX/ MTBE and other soluble monoaromatic hydrocarbons compounds. The most soluble of these compounds (including MTBE) will form the leading edge of the contamination plume. The residual pure product is held within the soil by capillary forces or physical barriers (for example pools of NAPLs overlaying clay shelves) and unless removed remains within the soil, acting as a long-term source of pollution.

Day *et al* (2001) summarised the physical, chemical and biological processes involved in the transfer and interactions of petroleum components within the subsurface environment (Figure 1.8).

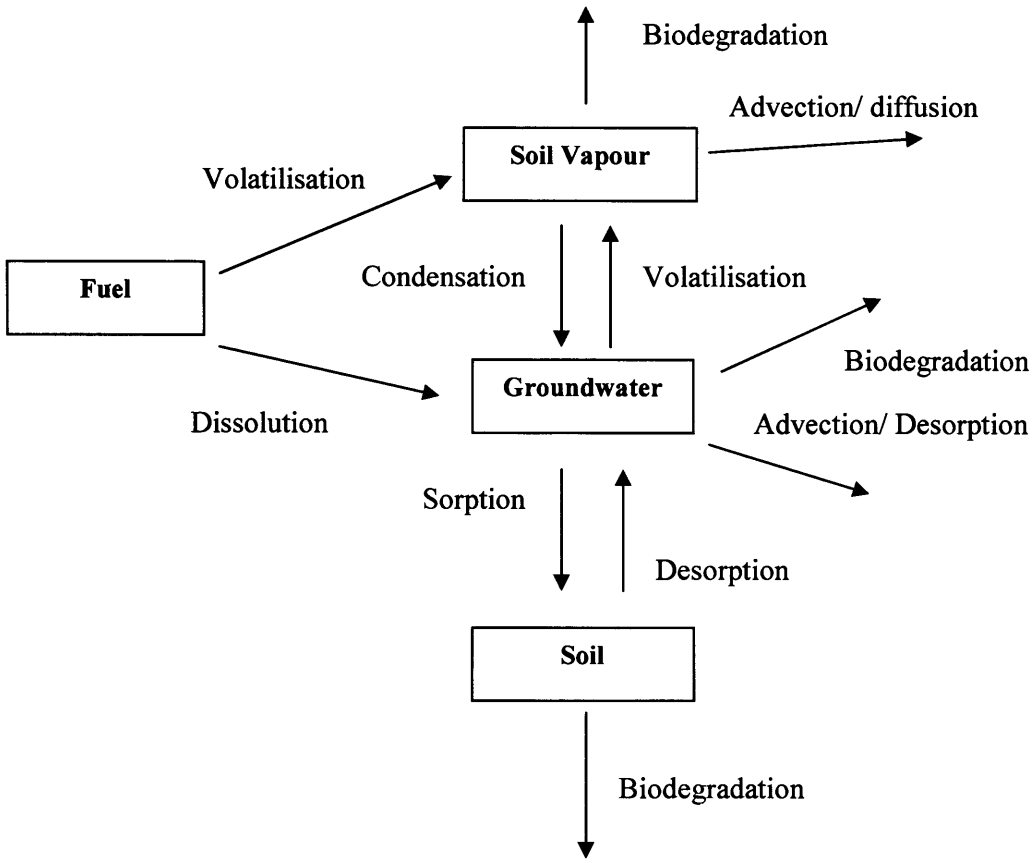


Figure 1.8. Transformations of Hydrocarbon States in Subsurface Environment. Source: Adapted from Day *et al,* 2001.

In general, compounds present in fuel oil that have low solubility, low volatility and strong adsorption characteristics will be found throughout the soil near a contaminated site or at physical barriers such as the water table. Compounds that are of high volatility will be found in the soil gases. The constituents of fuel oil that have a high solubility will be found within the aquifer.

1.3.5.2. Movement of Fuel Oil Compounds within the Aquifer.

Advection, dispersion, sorption and degradation are the processes that most strongly influence organic solute transport in saturated groundwater environments (Roberts *et al,* 1982). Advection is the transport of the solute at a velocity equivalent to that of groundwater movement. Dispersion is the spreading of a concentration as a result of spatial variation in aquifer permeability, fluid mixing and molecular diffusion. Sorption is defined as the retention of a solute in the soil phase by the partitioning between the aqueous phase and the solid phase.

Degradation is the utilisation of the organic solute by microorganisms, or the consumption of the compound in a chemical reaction with the aquifer solids, water, waterborne solutes or colloids. Each of these processes must be fully understood for a particular contamination situation, as it will give an indication of the movement of the fuel through the groundwater system.

Sites that have experienced petroleum contaminations show particular patterns in groundwater contamination (Deutsch, 1997). In the area nearest the source, oxidizable organic matter consumes oxygen (and other electron acceptors) within the aquifer, leading to the partial degradation of the fuel oil. During this process, aerobic heterotrophic microorganisms respire at the expense of the more labile hydrocarbons, consuming oxygen (Sufllta and Mormile, 1993). A localised anaerobic zone is produced because of the consumption of oxygen. This tends to mobilise Fe/ Mn and other metals into the aquifer, increasing their concentration in the water. Methanogenic conditions can prevail near the source if the aquifer cannot maintain the oxidising conditions. Biodegradation of the contaminant increases downstream of the anaerobic zone, as aerobic bacteria are able to utilise the increased oxygen concentrations. Fe and Mn then reprecipitate as the redox potential increases, lowering their concentrations in the ground water. Three parameters regulate the microbiological degradation of fuel oils, the temperature, the presence of nutrients and oxygen and the presence of adsorbed water. Aerobic conditions can lead to the total degradation of fuel oils, leading to the production of little or no transformation products that could have the potential to contaminate the groundwater further.

Given time and under the right conditions, aquifers have the ability to restore water quality after contamination with petrochemicals. However the time taken to restore an aquifer naturally may prove too long, and if left without the appropriate remediation technique could contaminate a potable water source.

1.3.5.3. The Movement of MTBE and BTEX within the Subsurface Environment.

Compared to other fuel constituents such as benzene, MTBE is highly water soluble (by one order of magnitude higher than benzene). MTBE has a solubility in water of approximately 4.8g/100g of water (4.8%). For this reason, MTBE is easily dissolved in soil and groundwater and is quickly transported from soil to

groundwater (Rong, 2001). Mitani *et al* (2002) stated that MTBE can travel throughout aquifers almost as quickly as the groundwater. Large volumes of MTBE released into the subsurface environment can be expected to migrate far into the groundwater system. Note that although BTEX compounds are much less soluble than MTBE, they are indeed more soluble than other fuel oil compounds and hence are likely to travel preferentially throughout the aquifer. Landmeyer *et al* (1998) suggested a chromatographic separation of MTBE with respect to BTEX compounds within groundwater aquifers, as MTBE was detected in wells downstream of a contaminant release before the BTEX compounds. The high solubility of MTBE is due to the dipolar nature of the compound (Burgess *et al,* 1998). With a specific gravity of 0.74 MTBE is less dense than water and can float on shallow aquifers. Another important consideration when considering the movement of MTBE in the subsurface environment is that it is poorly sorbed onto carbon based substrates. This means it will move quickly through the soil into the aquifers with negligible sorption. Because of the highly soluble nature of MTBE there is increasing evidence of contamination in storm water and shallow groundwater, from primarily diffuse (or non-point) sources (Hartley *et al,* 1999).

MTBE is a persistent compound once released into the subsurface environment due to the presence of the *t*-butyl group. The *t*-butyl group inhibits environmental degradation under normal conditions, and strongly inhibits natural biodegradation (Mitani *et al*, 2002).

Monitoring MTBE within groundwater may be of value as an indicator for the more serious consequences of a fuel spill.

In contrast to MTBE, ETBE and TAME are less mobile in groundwater as they are both approximately half as soluble in water.

1.3.5.4. High Ethanol Content Fuels

Adam *et al* (2002) stated that the risk of groundwater contamination with a gasoline-ethanol mix would be much higher than that of an incident caused by an ordinary gasoline mix. This is because of the increased solubility of gasoline components in ethanol. High ethanol fuels can cause greater downward migration throughout the soil. Adam *et al* (2002) also studied the effect of the downward migration of a diesel-ethanol fuel. The study concluded that ethanol

enhanced the movement of the diesel through a simulated subsurface environment. An aqueous ethanol concentration of 10% would be required for any movement to occur. A 25% aqueous ethanol solution mobilised the majority of the hydrocarbons, decreasing the retention time throughout the soil column. A solution of 50% ethanol caused the unimpeded movement of hydrocarbons throughout the column.

1.3.6. Case Study: Site X.

For legal reasons, the location of the site for the following case study is confidential. Data was provided by Campbell Reith Hill (CRH), and relates to a contamination incident that affected an Anglian Water abstraction borehole. The case study has been included in the chapter as it illustrates the behaviour of diesel fuel in the subsurface environment. Particularly it illustrates the localised biodegradation of certain fractions of the fuel, and the transport of the soluble aromatic fraction of the fuel.

The contamination incident at Site X occurred in 1998 when 15,000L of red diesel was lost via a corroded underground pipe leading to an UST. Once the incident was identified, a number of inspection boreholes were drilled surrounding the spillage site. In some boreholes up to 2"-3" of floating oil was detected on the surface of the groundwater. A number of monitoring boreholes were drilled to monitor the movement of the spillage towards the abstraction boreholes.

The study conducted by CRH and the BGS revealed that two processes occurred in the groundwater at Site X. This lead to the separation of diesel-based organic compounds within the groundwater. The processes are; biodegradation and selective solubility.

Two classes of hydrocarbons dominated the compounds found in the groundwater at Site X;

1) Aromatic compounds comprising mainly of C_{2-5} alkylated benzenes and C_{1-3} alkylated naphthalenes.
2) Normal alkanes (distribution range *n*-C_{10-22} maximising at *n*-C_{12} and *n*-C_{15}).

Note that the isoprenoids (branched hydrocarbons) pristine and phytane were the next most prominent compounds.

Selective Biodegradation at Site X.

CRH and the BGS demonstrated that diesel derived organics were being biodegraded at Site X. In general, straight-chained alkanes are more easily degraded than aromatics, which in turn are more easily degraded than isoprenoid and cyclic alkanes. Analysis by the BGS demonstrated the selective biodegradation of straight-chained *n*-C_{17-18} compounds with respect to pristane and phytane. They also showed that biodegradation was still ongoing in the most contaminated area. This was consistent with the utilisation of dissolved oxygen, nitrate and sulphate.

Fractional analysis of the hydrocarbons pointed to the preferential degradation of the fuel at the site. Diesel in its unaltered state generally contains 1.5% mineral range organics (MO – typically C_{20+} compounds) and 98.5% diesel range organics (DRO – typically C_{10-20} compounds). A more recent analysis of the hydrocarbons at Site X has seen a decrease of DRO to 75% and an increase of MO to 25%. This demonstrates selective biodegradation at the site.

Solubility of Diesel-Range Compounds at Site X.

A typical diesel fuel contains 2-3% water-soluble aromatics, the rest being made up of low solubility hydrocarbons. Analysis of the groundwater at Site X by the BGS estimated the hydrocarbon mixture to contain 57-85% water-soluble aromatics, most likely reflecting the greater solubility of the compounds. Also of interest was the fact that the concentration of the aromatic fraction (compared to other compounds), increased with distance from the zone of contamination. This suggested that the aromatic fraction of the fuel was transported downstream of the initial contamination area at Site X. Evidence for the long term transport of the soluble diesel derived aromatics was observed 1.8km down stream of the contamination point, which was estimated to contain 2.24μg/L total aromatics. In the case of the Site X data however, other possible sources of soluble hydrocarbon contamination have to be considered. For example the close proximity of an A road which is noted for its frequent accidents.

The Contaminant Plume at Site X.

The contamination plume observed at Site X is thought by the BGS to most likely be a 'pulse' of diesel, which has been 'smeared' into three specific zones. This contains;

1) An inner zone with the highest DRO concentration, which has moved away from the contamination point.
2) A middle zone in which biodegradation has occurred - as measured by higher pristane and phytane ratios.
3) An outer zone, where diesel derived aromatic hydrocarbons are being transported due to their higher water solubility.

Figure 1.9 illustrates the contaminant plume at Site X where UCM = unresolved complex mixture.

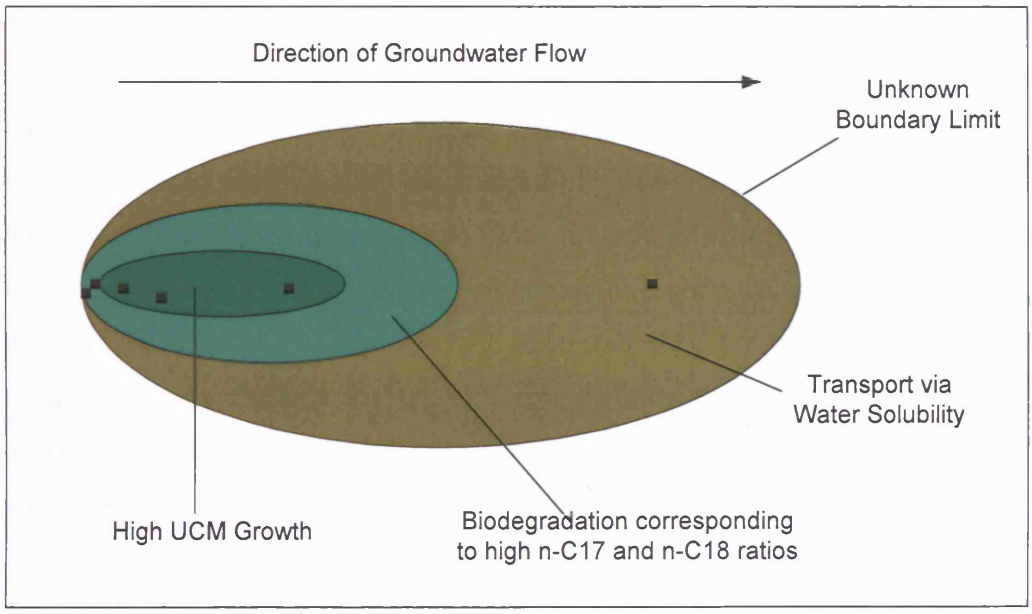


Figure 1.9. Contaminant Plume at Site X.

1.4. Groundwater Remediation.

The aim of this section is to introduce some of the remediation techniques that can be employed after the fuel oil contamination of the subsurface environment. Both in-situ and ex-situ remediation methods will be reviewed. As previously stated, the ex-situ remediation technologies investigated in this project (GAC Adsorption and Air-Stripping) will be looked at in more detail in sections 1.6 and 1.7 respectively.

1.4.1. Introduction to Groundwater Remediation.

The first thing that must be implemented in the remediation of a contaminated subsurface environment is the removal of the hydrocarbon source. This mass acts as a permanent source of subsurface contaminants and if not removed can cause a petrochemical plume to grow and persist (Mackay and Cherry, 1989). Physical methods of removing the organic mass include excavating the immediate area and removing the product for disposal. If petrochemical hydrocarbons reach the water table, they can sometimes be pumped out via boreholes.

Nyer and Skladany (1989) suggested that the in-situ or ex-situ remediation of fuel oil contamination must address the particular organic compounds present. In this way remediation can be thought of as the combined cleanup of several organic compounds each having different physical, chemical and biological properties. The USEPA (1998) also suggested that the overall effectiveness of the remediation method employed is directly linked to the chemical and physical characteristics of the constituent of interest. For these reasons the composition of the fuel oil involved in the contamination must first be established, as this will provide the most effective remediation solution for a specific site. Along with the composition of the fuel oil involved, if the remediation project is to provide a permanent cleanup, a detailed and accurate geological site characterisation will also be needed in order to increase the probability of overall success (Mackay and Cherry, 1989).

Marley *et al* (1992) stated that no single remediation technique could accomplish all the objectives of a complete site cleanup (either in-situ or pump and treat methods).

1.4.2. In-Situ Remediation.

1.4.2.1. Volatile Organic Carbon (VOC) Removal.

Marley *et al* (1992) suggested that the removal of VOCs from a recently contaminated area should be the primary consideration to ensure effective remediation of the site. Contamination of the soil lying beneath a spill acts as a potential long-term source of hazardous vapours in the vadose zone and dissolved VOCs in the groundwater. The vadose zone is the saturated area above the water table.

There are a number of in-situ remediation technologies that exist, which can be applied to clean up VOC contamination. These include;

Soil-Vapour Extraction (SVE).

In the SVE process, a pressure gradient is applied in order to induce airflow through the soil contaminated with VOCs. The air is drawn towards the vacuum causing an upset in the equilibrium between the VOC phase, the adsorbed phase, and the vapour phase. This leads to the enhanced partitioning of the VOC into the vapour phase, hence the compounds are removed from the soil. Nadim *et al* (2000) wrote that the removal VOC's from contaminated soil could be increased if steam is injected along with the air. An above ground treatment system (for example GAC adsorption) is sometimes needed in order to make sure the waste gases do not breach the relevant gaseous emission standards. Gerbasi and Memoli (1994) demonstrated that an integrated SVE strategy could lead to the effective remediation of a gasoline-contaminated site.

In-Situ Air-Sparging.

This process involves injecting a hydrocarbon free gaseous medium (usually air) into the saturated zone, below or in the contaminated area. The gaseous medium can be injected into contaminated groundwater via wells or trenches (Pankow *et al*, 1993). The VOCs partition into the gaseous medium, which travels upwards and can then be removed by soil vapour extraction. Air-sparging can be thought of as an in-situ air-stripping system. Contaminants that are easily stripped using traditional air-stripping techniques are considered to be amenable to in-situ air-sparging. Compounds susceptible to air sparging include the lighter petroleum compounds (C_3-C_{10}). The air-sparging of less susceptible compounds may be

enhanced if air, ozone and/or hydrogen peroxide is used as the injecting gas. This increases the oxidation of the semi volatile compounds, and also increases natural biodegradation.

1.4.2.2. In-Situ-Biodegradation.

The use of in-situ biodegradation in groundwater remediation is a well-documented procedure. The process usually involves stimulating indigenous microorganisms within the subsurface environment, although non-indigenous organisms can sometimes be used (Thomas and Ward, 1989). The contaminants are used as a food source and are subsequently degraded through the organism's metabolism. Stimulation can be achieved by the addition of nutrients and O_2 (the terminal electron acceptor). These are added directly to the subsurface environment. The microflora converts the organic waste into biomass and harmless by-products such as CH_4, CO_2 and inorganic salts. The process is very economical, but because it involves the use of living organisms can be affected by a number of environmental and geological conditions. Problems can also arise from regulatory authorities if non-indigenous microorganisms are used (Marley *et al,* 1992).

1.4.2.3. Natural Attenuation.

Kao and Prosser (2001) defined natural attenuation as a passive remedial approach that depends upon natural processes to degrade and dissipate contaminants in the soil and groundwater. The process of natural attenuation relies upon a number of natural processes including physical, chemical and biological transformations. Examples of such processes include aerobic/ anaerobic degradation, dispersion, volatilisation, oxidation, reduction and adsorption. Out of these chemical, physical and microbiological processes, aerobic and anaerobic biodegradation is thought to contribute most to the reduction of contaminants in a petroleum-contaminated groundwater. Aerobic microorganisms require dissolved oxygen as the terminal electron acceptor during biodegradation, whilst anaerobic degradation relies on a variety of mechanisms for electron transfer including; nitrate/ ferric iron (Fe^{3+}), sulphate and carbon dioxide.

In a study conducted by Kao and Prosser (2001) biodegradation accounted for 88% of the total BTEX removal at a gasoline spillage site.

Although natural attenuation is known to be very effective in the removal of fuel oil contamination from groundwater, procedures must still be put in place by water companies to protect borehole sources.

An example of natural attenuation in the passive remediation of a diesel contamination site can be seen in section 1.3.6.

1.4.2.4. Pump and Treat.

Technologies such as advanced oxidation/ air-stripping and adsorption can be applied at the site of a contamination as in-situ remediation techniques. The contaminated groundwater is extracted via boreholes, and the technologies are applied aboveground. The technologies employed are the same as those implemented in section 1.4.3. The only difference being the placement of the technology.

Nadim *et al* (2000) suggested that pump and treat techniques were usually accompanied by in-situ vapour extraction technologies, in order to enhance the removal of the hydrocarbons from the subsurface.

1.4.3. Post-Abstraction Remediation Techniques.

Taking into account the local geological conditions and specific fuel oil released into the subsurface environment, soil remediation (effectively VOC removal) and free product removal at the contaminant source will not always prevent the need to treat the underlying groundwater post-abstraction. Although appropriate in-situ techniques would need to be implemented to reduce the risk of groundwater contamination, a method for removing the contaminant from the aquifer, or after it has been extracted at the borehole must be employed to safeguard the quality of the water.

Biodegradation.

Biodegradation has recently been considered for the post-abstraction removal of MTBE and BTEX compounds from contaminated gourndwater.

Pruden *et al* (2003) suggested that fluidised bed reactors (FBRs) could be effectively used to remediate MTBE and BTEX compounds. FBRs utilise GAC

as a biological attachment medium, where biomass retention is high due to the extensive surface are of the carbon. It was suggested in the studies carried out by Pruden *et al* (2003) that effluent concentrations of MTBE and BTEX were comparable. In turn this suggests that BTEX did not inhibit the degradation of MTBE. Removal rates for MTBE ranged up to 99.76% and removal rates for benzene ranged up to 99.93%.

However, the use of biodegradation as a remedial method for contaminated drinking water has not yet been fully investigated.

Air-Stripping, Adsorption and Advanced Oxidation Processes (AOPs).

Adsorption using GAC, air-stripping and AOPs are examples of common post-abstraction remediation techniques. The technologies are also extensively used within the water industry for general water treatment purposes.

1.5. MTBE and BTEX Remediation Techniques.

The USEPA suggested that the effectiveness of a remediation method is directly linked to the physical and chemical characteristics of the compound of interest (USEPA, 1998).

If the MTBE concentration at a particular site is low enough that it is not of a significant environmental concern, the remediation technique will concentrate on the removal of other compounds such as BTEX. However if there are significant concentrations of MTBE, then this will be the driving force behind the remediation technique (USEPA, 1998).

From a review of the current literature detailed in this section it is apparent that there are three common (post-abstraction) remediation processes used to remove MTBE and BTEX from contaminated groundwater; adsorption, air-stripping and advanced oxidation processes (AOPs). Other post-abstraction remediation technologies include biodegradation and membrane processes.

This section of the literature review begins with an overview of MTBE and BTEX remediation and is followed by a section of the fundamentals of air-stripping, adsorption and AOPs. Finally the effectiveness, efficiency and capacity of air-stripping, adsorption and AOP technologies in the removal of MTBE and BTEX are presented.

It is apparent from a review of current literature that due to the political, health and scientific uncertainties surrounding MTBE, recent literature has focused on the remediation of MTBE rather than BTEX compounds. For this reason the MTBE remediation is referred to more than BTEX compounds within this chapter.

1.5.1. Overview of MTBE Remediation.

Mitani *et al* (2002) stated that due to MTBE's unique physicochemical properties, the compound would require new and novel treatment approaches. MTBE's unique physicochemical properties strongly depend upon the hydrophilic nature of the compound (Keller *et al*, 2000). The polar oxygen atom within MTBE causes the compound to be much more hydrophilic than alkanes and aromatic compounds such as BTEX (Davis and Powers 2000).

MTBE's high water solubility, low Henry's Law constant and low organic carbon partition coefficient are indicative of the hydrophilic nature of the

compound. Hence treatment options that rely upon the hydrophobic nature of compounds are generally ineffective in removing MTBE from contaminated water.

A review of the current literature has suggested conflicting ideas on which of the common remediation methods should be employed to treat an MTBE contaminated groundwater.

Shih *et al* (2002) suggested that MTBE could be removed from drinking water through several techniques including; air-stripping, adsorption and AOPs. It was suggested that MTBE removal using air-stripping would not be cost effective and that over six times air-to-water ratios would be required for the treatment of MTBE contaminated drinking waters, compared to other fuel oil compounds such as BTEX. The study suggested that advanced oxidation using ozone or ozone/ peroxide could be effective in removing MTBE, however, hazardous by-products including bromate were produced and therefore had to be removed in an additional treatment step. Shih *et al* (2002) based their MTBE work on GAC adsorption, as this was a proven technology for taste and odour causing organics and synthetic organic chemical contaminated drinking water.

Annesisi *et al* (2000) suggested that MTBE could be removed from wastewater using biodegradation, air-stripping, AOPs, adsorption and membrane processes. However it was suggested that adsorption onto solids was regarded as one of the most dependable and effective technologies, characterised by a relatively low cost.

Annesisi *et al* (2000) suggested that alternative adsorbents (e.g. the carbonaceous resin amberlite XAD4) could be employed to remove MTBE and its by-product TBA. Unlike GAC, alternative adsorbents can be easily regenerated.

Chang and Young (2000) suggested that the removal of MTBE using activated carbon or air-stripping (commonly employed to remove other organic compounds), is costly because of MTBE's high solubility and low Henry's Law constant. It was also suggested that MTBE has proven resistant to oxidation in many common water treatment operations including exposure to 254 ultraviolet light.

Sutherland *et al* (2004) investigated the treatability of MTBE in five groundwater sources using air-stripping, GAC adsorption and advanced oxidation using O_3/H_2O_2 and UV/H_2O_2. The study suggested that air-stripping had the lowest

treatment costs for high influent flow rates (>3800 L/min), however, relatively tall towers would be needed to achieve the desired removal targets. At low flow rates (~38 L/min) advanced oxidation provided the lowest treatment costs for four of the five groundwaters tested within the study. When the groundwater was subject to high chemical oxygen demand (COD), advanced oxidation was found to be ineffective. Adsorption of MTBE using GAC was found to be effective at most conditions, although it represented the most costly remediation option.

Keller *et al* (2000) stated that the cost of treating MTBE-contaminated water using GAC or air-stripping technology, was 40-80% higher than waters contaminated with other hydrocarbons such as benzene.

1.5.2. Overview of BTEX Remediation.

Due to the physical and chemical properties of BTEX compounds, the remediation of contaminated groundwater through adsorption, air-stripping and AOP technology is much more effective than that of MTBE.

In general the properties which make BTEX compounds more amenable than MTBE to remediation are;

- Lower water solubility
- Higher volatility

The physical and chemical properties of BTEX are presented in Chapter 1.3.2.2.

Throughout literature it is stated that VOC compounds (including BTEX) are amenable to adsorption, air-stripping and AOP. For example;

- Shih *et al* (2003) suggested that sorption (in particular adsorption using GAC) is a proven technology for treating contaminated water for many different organic pollutants including BTEX.
- Giffin and Davis (1998) suggesed that GAC is a proven technology for the removal of BTEX compounds from contaminated groundwater.
- Nirmalakhandan *et al* (1993) stated that counter-current air-stripping processes were identified by the US Government as the best available technology (BAT) for removing volatile organic compounds from contaminated groundwater.

- Holden and Tunstall-Pedoe (1998) suggested that air-stripping was effective at removing most organic contaminants including BTEX compounds.
- Chang and Young (2000) suggested that very high removal rates (99.9%) of benzene could be achieved using AOPs.

1.6. Principles of Air-Stripping, Adsorption and AOP.

The following section details the fundamental principles of air-stripping, adsorption and AOPs. These principles are then applied to the remediation of MTBE and BTEX compounds in section 1.7.1 – 1.7.3.

1.6.1. Air-Stripping (Aeration).

Air-stripping is a process in which water and air are brought into contact with each other for the purpose of transferring volatiles from the water to the gaseous phase (Dyksen and Hess, 1982). The technique of air-stripping (sometimes referred to as aeration) has been extensively used as a technique for the removal of taste and odour producing compounds, as well as in the removal of trace organic compounds within water treatment. The mechanism by which organic compounds are effectively transferred from solution to a gas is the concentration gradient of the solute-gaseous system. A concentration gradient will always transfer the substance in a direction that will equalise concentrations, and hence destroy the gradient.

The effectiveness of air-stripping in drinking water treatment has been known for some time. Roberts *et al* (1985) stated that counter-current air-stripping towers have been shown to be effective in controlling trace organics (including VOCs).

1.6.1.1. Henry's Law Constant within Air-Stripping Theory.

The principles of Henry's Law Constant are discussed in section 1.3.4.1. The following section describes how the principles are applied to air-stripping.

Keller *et al* (2000) stated that the VOC removal efficiency of an air-stripper is a function of the design of the unit, along with the Henry's Law Constant of the compound.

Munz and Roberts (1987) also stated that the Henry's Law Constant was a major factor in determining the degree of transfer during counter-current packed columns, along with the mass transfer coefficient (K_La) of the compound.

As previously presented in Chapter 1.3.4.1, Henry's Law states that the amount of gas dissolved in a given quantity of liquid (at constant temp and total pressure) is directly proportional to the partial pressure of the gas above the solution. Hence Henry's Law can be considered the partition coefficient that describes the tendency of a compound to separate between the gas and the liquid at equilibrium (Dyksen and Hess, 1982). The greater the Henry's Law constant, the greater the driving force for transfer of the solute from solution to the gaseous phase (Roberts *et al,* 1982). The greater the hydrophobicity of a solute (measured by its octanol:water partition coefficient), the greater the value of its Henry's Law Constant and the more easy the compound will be removed by air-stripping. This is because the compound favours the gaseous state.

Hung *et al* (2002) stated that although MTBE has a relatively high vapour pressure compared to that of benzene (MTBE is roughly three times as volatile as benzene), this is offset by the fact that MTBE prefers to remain in water. MTBE has a much lower Henry's Law Constant than BTEX compounds and hence will be less amenable to removal by air-stripping.

Munz and Roberts (1987) studied the effect of increased temperature on the Henry's Law constant of various organic compounds. The study concluded that the Henry's Constant increased by a factor of 1.6 with each 10°C rise in temperature - this represents a very strong effect. Temperature therefore is likely to be the most important factor in determining the extent of volatile solutes removal in gas-liquid contacting systems.

Stover and Kincannon (1983) suggested that VOCs with Henry's Law constants from 0.0045 – 0.04 may require higher temperatures in order for the compound to be amenable to air-stripping. According to Stover and Kincannon (1983), MTBE would require higher temperatures to be effectively stripped.

Munz and Roberts (1987) studied the effect of cosolvency on the Henry's constant for organic compounds. The study concluded that only very high cosolvent concentrations in excess of 10g/L would lead to a reduction in a Henry's Constant.

1.6.1.2. Rate of Mass Transfer and the Mass Transfer Coefficient.

The rate of mass transfer within the air-stripping process depends on a number of internal factors. It is represented by the following equation, which can be found throughout literature (for example Dyksen and Hess, 1982 and Nirmalakhandan *et al*, 1987);

$$M = K_L a\, P \qquad \textbf{(eqn 1.5)}$$

Where M = mass of substance transferred per unit time and volume, K_L= coefficient of mass transfer, a = effective area and P = concentration difference. The mass transfer coefficient ($K_L a$) is the product of the overall liquid mass transfer coefficient and the specific interfacial area (Ball *et al*, 1984). The mass transfer coefficient must be maximised when designing aeration equipment, as this will ensure optimum conditions for air-stripping. It was suggested in literature (e.g. Ball *et al*, 1984 and Kavanaugh and Trussell, 1980) that the mass transfer coefficient should be estimated using pilot studies. The mass transfer coefficient is specific to the particular application hence it will depend upon numerous variables including; packing type (and hence cross-sectional area), range of contaminants requiring removal, temperature and the air-to-water ratio.

However, Dzombak *et al* (1993) stated that the mass transfer coefficient could be estimated using the Onda Model. Indeed there are other models for estimating the mass transfer coefficient. Refer to Chapter 3.2.1.2 for estimation of mass transfer coefficient for an air-stripping unit.

Nirmalakhandan *et al* (1987) suggested that the rate of stripping VOCs would increase with greater air-to-water ratios (effectively the driving force behind mass transfer). However, as the air-to-water ratio increases so does the energy costs. Thus there will be a point at which the increase in costs due to greater air-to-water ratios will outweigh the benefit from increased mass transfer.

1.6.1.3. Air-Stripper Design Theory.

Although the equations presented in this section are typically used to design air-stripping columns, the theory behind the equations aid the understanding of the air-stripping process.

Literature cites four equations for the design of air-stripper units, based on mass transfer theory. The equations can be found in chemical engineering handbooks and other literature such as; Ball *et al*, 1984 and Dzombak *et al*, 1993.

The height of a packed tower can be calculated by the following equation;

$$Z = (HTU)(NTU) \qquad \textbf{(eqn 1.6)}$$

Where Z = total packing height (m), HTU = height of mass transfer unit (m), and NTU = number of transfer units (dimensionless).

HTU can be calculated by;

$$HTU = \frac{L}{K_L a} \qquad \textbf{(eqn 1.7)}$$

Where L = liquid loading rate ($m^3/m^2\ h^{-1}$), $K_L a$ = mass transfer coefficient (h^{-1}). The mass transfer coefficient is a product of the overall liquid mass transfer coefficient K_L (m/h), and the specific interfacial area a (m^2/m^3).

NTU can be calculated by;

$$NTU = \frac{R}{R-1} \ln \frac{C_{in}/C_{out}(R-1)+1}{R} \qquad \textbf{(eqn 1.8)}$$

Where C_{in} = concentration of contaminant in influent (μg/L), C_{out} = concentration of contaminant in effluent (μg/L), and R = stripping factor (dimensionless).

The stripping factor R can be calculated by;

$$R = H \times G/L \qquad \textbf{(eqn 1.9)}$$

Where H = Henry's Law Constant (unitless), L = liquid loading rate ($m^3/m^2\ h^{-1}$) and G = air loading rate ($m^3/m^2\ h^{-1}$).

Referring to equation 1.7, the calculation of HTU requires the mass transfer coefficient for the particular application.

The mass transfer parameter incorporates the chemical properties of the compound (Henry's Law Constant, solubility and diffusivity), properties of the packed tower (e.g. interfacial area and liquid and gas loading rates) and the properties of the liquid being decontaminated (e.g. temperature and quantity of liquid) (Sutherland *et al*, 2004).

When mass transfer coefficients cannot be determined experimentally, empirical equations can sometimes be implemented. One example of such an equation is the Onda correlation. The Onda correlation takes into account both the liquid and gas phase resistances to mass transfer and has been extensively validated throughout literature for use in VOC removal (Nirmalakhandan *et al* 1987).

The overall mass transfer coefficient is presented in equation 1.10;

$$(K_L a)^{-1} = (k_L \cdot a_w)^{-1} + (H \cdot k_G \cdot a_w)^{-1} \quad \textbf{(eqn 1.10)}$$

Where H = Henry's law constant (unitless), k_L = liquid phase mass transfer coefficient (m/s), k_G = gas phase mass transfer coefficient (m/s) and a_w = wetted area of packing material (m^2/m^3). k_L, k_G and a_w are estimated separately;

$$a_w/a_t = 1\text{-}\exp\left(-1.45\,[\tau_p/\tau_L]^{0.75}[L/a_t\mu_L]^{0.1} \times [L^2 a_t/p_L^2 g]^{-0.05}\,[L^2/p_L \tau_L a_t]^{0.2}\right) \quad \textbf{(eqn 1.11)}$$

$$k_L = 0.0051[\mu_L g/p_L]^{1/3}\,[L/a_w\mu_L]^{2/3} \times [\mu_L/p_L D_L]^{-0.5}[a_t d_p]^{0.4} \quad \textbf{(eqn 1.12)}$$

$$k_G = 5.23[a_t D_G][G/a_t \mu_G]^{0.7} \times [\mu_G/p_G D_G]^{1/3}\,[a_t d_p]^{-2} \quad \textbf{(eqn 1.13)}$$

Where a_t = total surface area per unit volume of packing (m^2/m^3), τ_p = critical surface tension of steel (N/m), τ_L = surface tension of water (N/m), μ_L = viscosity of water (Nsm^{-2}), μ_G = viscosity of air (Nsm^{-2}), p_L = density of water (kg/m^3), p_G = density of air (kg/m^3), D_L = diffusivity of solute in water (m^2/s), D_G = diffusivity of solute in air (m^2/s), d_p = nominal diameter of packing material (m), L = molar flow rate of water (mol/s), G = molar flow rate of air (mols/s) and g = acceleration due to gravity (m/s^2).

In a study conducted by Roberts *et al* (1985) on the air-stripping removal of VOCs, it was suggested that packing height Z had relatively little effect on the observed $K_L a$ values. Indeed referring to equations 1.10 – 1.13 it is expected that $K_L a$ values should be independent of Z. Laboratory data collated in the Roberts *et al*, 1985 study confirmed that for the most volatile compounds, Z did not affect the magnitude of the mass transfer coefficient.

The Roberts *et al*, 1985 study also suggested that for the most volatile compounds, $K_L a$ was independent of the air flow rate. For less volatile solutes, the observed $K_L a$ decreased with decreasing air flow rates. The influence on the decreasing $K_L a$ values with decreasing air flow rates correlated with the decrease in volatilities of the respective compounds.

Referring to equations 1.10 – 1.13, $K_L a$ values should increase with increasing water flow rates. This was confirmed in the Roberts *et al*, 1985 study where

increases in water flow rates correlated with increases in K_La values for the most volatile compounds, whilst the dependence on K_La values was weaker for less volatile compounds.

Nirmalakhandan *et al* (1987) stated that the required given removal efficiency for a specific compound can be achieved by different combinations of the following design parameters; height of packing, air-to-water ratio, hydraulic loading rate, pressure drop of the system and packing type. Different combinations of all these factors can lead to a multitude of air-stripper designs, each with their unique capital, operating and overall treatment costs. Site-specific conditions such as the cost of the electricity, or the installation of the towers themselves must also be considered when predicting overall treatment costs of an air-stripper unit.

Nirmalakhandan *et al* (1993) also stated that even though the design procedure of air-stripping systems is well documented and relatively easy to follow, the optimisation of a full-scale process is not as straightforward due to the large number of variables involved.

1.6.1.4. Considerations in the Design of Air-Stripping Systems.

Coulson and Richardson (1983) suggested that the design of packed columns should follow the following guidelines;

1) Select the type and size of packing.
2) Determine the height required for specified separation.
3) Calculate column diameter to handle the liquid and gas flow rates.
4) Select the appropriate column internals (support plates/ nozzles etc).

Pressure Drop and Flooding throughout the Column.

It is imperative that when designing air-stripping units the pressure drop of the system must be investigated. The pressure drop through a column can have economic consequences to the unit. The pressure drop of a gas rising counter-current to liquid flowing through a packed tower can be represented graphically, and can be found in commercial literature and chemical engineering reference books (Kavanaugh and Trussell, 1980, Coulson and Richardson, 1983, Perry and Green, 1984). Kavanaugh and Trussell (1980) suggested that for a given liquid loading rate, gas pressure drop increases approximately in proportion to the square of the gas velocity. At high air-flow rates, liquid may be prevented from

flowing downwards normally by the rising gas. The liquid in this case has become entrapped – a term is called tower flooding. Tower flooding is a severe limiting factor in the efficient running of air-stripping towers, and is caused by the increased pressure drop (Freiburger, *et al*, 1993).

Packed towers should be designed to operate well below flooding conditions. Treybal (1980) suggested that air-stripping towers are usually designed for gas pressure drops of 200 to 400 N/m^2 per metre of packing.

Off-Gas Treatment.

Keller *et al* (2000) stated that adsorption units (usually GAC) will usually be needed to remove the VOCs from the gas stream. Local atmospheric emissions regulations must be adhered to - in the UK this is set by the EA. Based on mass balance, the mass flow rate of individual compounds within the gaseous effluent stream can be calculated by;

$$M = Q(C_{in} - C_{out}) \qquad \textbf{(eqn 1.14)}$$

Where M = mass flow rate, Q = volumetric flow rate, and C_{in} and C_{out} = influent and effluent water concentrations.

1.6.1.5. Counter-Current Air-Stripping Equipment.

There are a number of different designs of air-stripping equipment. Although counter-current packed columns are still the most widely used air-stripping units within the water industry - other units such as membrane, cascade and cascade-crossflow air-strippers can offer advantages such as reduced packing height, reduced pressure gradients and improved removal efficiency. Alternative units have not yet been investigated for the removal of fuel oil contaminants from groundwater.

Packed-Columns.

Within packed-columns, water effectively flows down through a column (under the influence of gravity), whilst air is forced upwards against the flow of the water.

Perry and Green (1984) stated that a typical packed column consists of a cylindrical shell containing a support plate for the packing material. Packing material held within the column can either be random or structured. Packing

materials in counter current packed columns provide high void volumes and allow maximum surface area. This design results in the continuous contact of air and water and minimises the thickness of the layer of the water on the packing, hence improving mass transfer (Dyksen and Hess, 1982). Devices can be added to the column to redirect water that may channel down the wall.

Other column internals include packing support plates and liquid redistribution plates, as well as the air and water nozzles.

Coulson and Richardson (1983) suggested that performance of the counter-current column is dependent upon the maintenance of good liquid and gas distribution throughout the packed bed. Hence the liquid and gas distribution is an important consideration in packed column design.

Figure 1.10 illustrates a simplified counter-current air-stripping column.

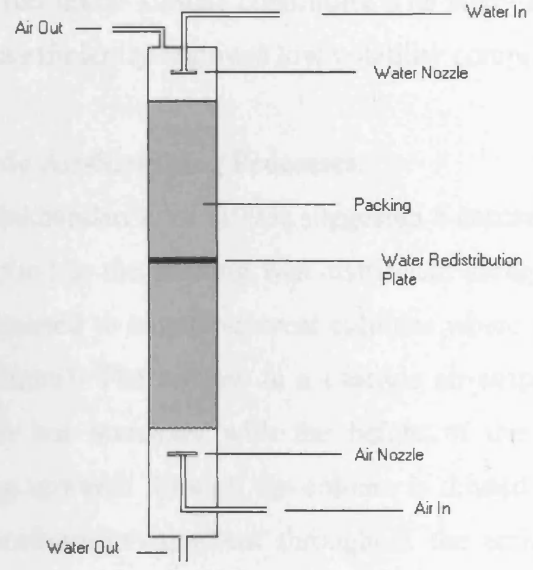


Figure 1.10. Simplified Counter-Current Air-Stripping Unit.

Counter-current air-stripping columns suffer from the disadvantage that air and water flow rates are limited by column flooding (Mertooetomo *et al*, 1993).

Alternative Air-Stripping Methods.

Membrane Air-stripping.

Membrane air-stripping works on the same principle as packed towers, where volatile organics are stripped from aqueous solution due to a difference in concentration gradient between the compound in the solution and the gas (Zander *et al,* 1989). The contact area in the membrane system is provided by air filled pores that cover the surface of a hydrophobic membrane. A high stripping rate of volatile compounds is assured because the hollow fibre shape of the membrane provides a large specific surface area.

In studies conducted by Zander *et al* (1989) mass transfer coefficients for a pilot scale membrane system removing various VOCs (including benzene), were found to be an order of magnitude greater than that of compounds in a packed tower run under similar conditions. The study also reported that the membrane process efficiently removed low volatility compounds.

Cascade Air-Stripping Processes.

Nirmalakhandan *et al* (1993) suggested a cascade air-stripping process in which air applied to the packing was distributed along the entire length of the column (as supposed to counter-current columns where air is only applied to the base of the column). The airflow in a cascade air-stripper is low at the bottom of the column but increases with the height of the column. The contaminated air moving upwards through the column is diluted with fresh air, thus maintaining the concentration gradient throughout the entire column. As mass transfer is maintained throughout the entire process, shorter packing depths are required for a desired efficiency. Energy requirements are also reduced due to a lower pressure drop.

1.6.1.6. Packing Types.

Coulson and Richardson (1983) stated that the principal requirements of any type of packing (random or structured) are that it should;

1) Provide a large surface area - thus producing a high interfacial area between the gas and the liquid.
2) Have an open structure. This means it will have low resistance to gas flow.

3) Promote a uniform distribution of the liquid on the packing surface.
4) Promote uniform gas flow across the column cross-section.

There are many diverse types and shapes of packing and have been designed to satisfy these requirements. They can be divided into two broad classes;

1) Random packings such as rings and saddles. These are dumped into the column and take up random arrangements.
2) Structured packing or those with a regular geometry such as stacked rings or grids.

Data required for the design of counter-current columns with respect to packing efficiencies can be found in general chemical engineering books (for example Perry and Green, 1984 and Coulson and Richardson, 1983), and commercial literature.

Random Packing.

There are many types of random packings on the market. These include; Raschig rings, Pall rings, Berl saddles, Intalox saddles, metal Hypac and Super Intalox, where each of these packing materials can be regarded as an improvement in both efficiency and liquid distribution respectively. Rings and saddle packings can be manufactured from a variety of materials: ceramics, metals, plastics and carbon. Metals and plastics (polypropylene) rings are more efficient than ceramic rings, because it is possible to make the walls thinner. Essentially, the material of construction will be determined by the particular application.

As far as economics are concerned, Raschig rings are cheaper per unit volume compared to Pall rings or saddles, but are less efficient and the total cost of the column will usually be higher. Because of weight and cost considerations, plastic packing is usually used in the water industry.

Structured Packing.

The term structured packing refers to packing elements made up from wire mesh or perforated metal sheets. The material is folded and arranged with a regular geometry, to give a high surface area with a high void fraction.

The cost of structured packing compared to random packing is higher, but this can be offset by their higher efficiency. A more efficient packing will be more

economical as lower air-to-water ratios will be needed. Also, the height of the tower associated with a more efficient packing will be less.

1.6.2. Adsorption.

Adsorption has been used in municipal water treatment for many years and is a proven technology. Activated carbon is the most widely used adsorbent in water treatment and is found in either dispersed powder form (PAC) or in fixed bed granular form (GAC) Casey, 1997.

McCabe *et al* (2001) stated that carbon adsorbents are commonly used in municipal water treatment works to remove trace organics from water, hence improving taste and reducing the chance of toxic compounds being formed in the chlorination step.

1.6.2.1. Definition of Adsorption.

Separation through adsorption occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly onto the surface of a substance than others. A sieve effect can also be caused if pores are too small to admit larger particles (McCabe *et al*, 2001). The adsorbate is usually held strongly enough to permit the complete removal of that compound from the fluid.

Adsorption was defined by Casey (1997) as a process in which solute molecules (the adsorbate) become attached to a solid surface under the attracting influence of surface forces such as van der Waals forces, hence adsorption is primarily a surface phenomenon. Hydrophilic substances and ions are not usually susceptible to adsorption.

1.6.2.2. Structure of Adsorbents.

An adsorbent, whether it is carbonaceous, inorganic, synthetic or naturally occurring must have an extremely large and accessible internal surface area in order for it to be technically proficient in removing trace substances in a separation process (Crittenden, 1998). The adsorption media must be relatively free of other adsorbed materials. Adsorbents must also have the ability to resist attrition, and have the ability to transfer the adsorbate materials quickly onto the adsorption sites.

The internal surface area of a commercial adsorbent is usually in the region of 300 – 1200 m^2 /g. The internal surface area of an adsorbent is governed by the size of the pores within the media. It is the pore size of an adsorbent that dictates which materials can be adsorbed. In carbons, silica gels and alumina, pore sizes are classed in three groups; micropores/ mesopores or macropores. Table 1.12 illustrates the classification of pore sizes.

	Size (nm)
Macropores	> 50
Mesopores	2 – 50
Micropores	< 2

Table 1.12. Classification of Pore Sizes within Adsorbents. Source: Crittenden, 1998.

Throughout activated carbon (and other materials), the degree of connectivity and ratio of these pores can vary widely; this leads to a potentially large number of materials that they can adsorb. In contrast, zeolites have very specific pore sizes and hence are very specific in which materials they can remove during the adsorption process.

1.6.2.3. Activated Carbon.

Although GAC is a more expensive treatment option than (for example) PAC in removing organics from water, it is able to remove a much broader range of chemicals, these include; taste-and-odour contributing compounds, total organic carbon (TOC), volatile organic compounds (VOC) and synthetic organic carbons (SOC).

There are many definitions of active carbon. Jankowska (1991) defined active carbon as a processed material with a highly developed porous structure and a large internal specific surface area consisting principally of carbon (87 to 97%), but also containing the elements hydrogen, oxygen, sulphur and nitrogen. The surface of an active carbon is usually non-polar and hydrophobic, with an affinity for organic molecules (Crittenden, 1998). Karanfil and Kilduff (1999) stated that it is the surface functional groups that influence the adsorption properties and the

reactivities of the carbon. These groups may include carboxyl, carbonyl, phenols, enols, lactones and quinines.

Dyksen and Hess (1982) stated that two properties of organic compounds influence adsorption by activated carbon;

1) Solubility – the less soluble the compound of interest, the better it is adsorbed.
2) Affinity – the greater the specific attraction between the solute and the GAC, the better the adsorption.

Increased molecular weight, decreased polarity, decreased ionic character, low pH for organic acids or high pH for organic bases, all decrease the solubility of the compound and hence increases the potential for adsorption. Compounds with high molecular weights are generally adsorbed more readily than compounds with lower molecular weights.

Karanfil and Kilduff (1999) suggested the current understanding of the forces affecting adsorption as being;

1) **Physical Interaction**. This includes size exclusion and microporosity effects. Size exclusion is thought to control the access of molecules to the finer pores, where the majority of the surface area for adsorption occurs. Increasing microporosity increases the adsorption of low molecular weight molecules. Multiple contact points and the overlapping of surface forces are caused when the dimension of the molecule is equal to that of the carbon pore.
2) **Chemical Interaction**. These interactions involve the chemistry of the carbon surface, the adsorbate and the solvent. The interactions can be significant for both large and small organic molecules. Adsorbates may interact with the carbon surface, including the basal plane electrons, unpaired electrons located on the edges of the terminal basal planes, and surface functional groups. These groups can influence the polarity of the surface of the carbon, and hence the interaction with the solvent.

GAC has the ability to adsorb materials from both the gaseous and liquid phases. Raw materials for the production of activated carbon include coals, peat, lignin, wood, refinery residuals and nutshells (e.g. coconut shells).

There are two types of activation processes - gas and chemical. The gas activation step involves heating the material in the absence of air at 400-500°C. This process drives off any volatile materials and develops small pores. Activation is then carried out with steam at 800-1000°C. The activation process selectively removes carbon, resulting in an opening of closed pores and an increase in size of the micropores. Chemical activation is carried out using zinc chloride or phosphoric acid in a one-stage step. Physical activation is more commonly used for the carbons used for chemical treatment. Chemical activation tends to produce carbons with larger pores than those produced from steam activation.

When deciding on which carbon to use for a particular application, a number of specific characteristics are used by GAC manufacturers to describe its structure and hence intended use (Calgon Application Bulletin, 2000);

- The magnitude of **adsorption forces** within a carbon is directly related to the amount and orientation of the graphitic plates surrounding the pore. High-energy pores are surrounded by large numbers of graphitic plates, and hence have high adsorption forces. Fewer graphitic plates surround low energy pores. The distribution of high and low energy pores is dependent on the raw material and the activation process. Low energy pores are best used to adsorb compounds of high concentration and which are easily adsorbed (low solubility/ high molecular weight). High-energy pores are best used to adsorb compounds at trace concentrations, which are also difficult to adsorb.
- The **trace capacity number** is used to measure the adsorptive capacity of a carbon. The trace adsorptive capacity is measured in milligrams of acetoxime per cubic centimetre of carbon. Activated carbons with high trace capacity numbers will be suited towards low concentration applications.
- The **iodine number** is also used when characterising the adsorptive capacity of a carbon. Iodine is easily adsorbed by GAC and the iodine number relates to the specific volume of the pores within the carbon. Hence the iodine number is not useful when trying to describe the capacity of a carbon to adsorb trace compounds.

A good understanding of the role of GAC surface chemistry on adsorbate uptake is critical in the selection, design and production of new adsorbents for the removal of organic compounds from drinking water supplies.

1.6.2.4. Other Adsorption Media.

Powdered Activated Carbon (PAC).

PAC is primarily used to treat surface water for seasonal variations in taste and odour. PAC can be added to the treatment process at different stages, these include; the intake, rapid mix, flocculation basin influent and filter influent (Pontius, 1990). The effectiveness of PAC is usually water specific, hence extensive bench and pilot tests should be performed to find the most effective PAC for the job.

Even though PAC has been used extensively for taste and odour control, little attention has been given to the use of PAC in the removal of volatile organics (Najm *et al,* 1991). Advantages of PAC are that it has a low capital cost, and that it can be applied only when needed. Disadvantages of the use of PAC include the fact that it is difficult to apply in a way that will utilise its full adsorptive capacity.

Najm *et al* (1990) showed that PAC performance could be significantly increased by reducing the PAC particle size, but that the rate of adsorption was significantly decreased when naturally occurring humic substances were present in the groundwater.

Activated Alumina (AA).

AA has been used in the past to remove inorganic substances from water. It has been suggested that AA could also be used to remove certain organic substances for example organic acids, surfactants and dissolved humic substances (Chen *et al,* 1989). There is no mention in the literature of AA being used directly to remove petrochemical hydrocarbons from water.

Chen *et al* (1989) found that the use of AA before GAC, combined with the in-situ regeneration of the AA, resulted in an 80% higher capacity of GAC for certain organic micropollutants, from solutions with high concentrations of humic substances. The AA had removed the background humic substances,

apparently reducing the competition for adsorption sites on the GAC. The removal of dissolved humic substances by AA is improved by preoxidation with ozone or hydrogen peroxide.

Synthetic Resins.

The use of synthetic resins in the removal of MTBE from water is currently an area of interest within literature. Due to the physical properties of MTBE, it is known that the compound is not very amenable to GAC adsorption. Work is therefore being carried out test the adsorptive capacity of alternative media (i.e. synthetic resins).

Studies on the adsorptive capacity of alternative adsorbents and resins are detailed in section 1.7.2 of the literature review.

1.6.2.5. Predicting GAC Performance.

It is imperative that the theoretical and kinetic performance of GAC is known before it is used for specific applications within the water industry.

1.6.2.5.1. Adsorption Equilibria and Adsorption Isotherms.

Within the adsorption process, the adsorption of aqueous material proceeds until there comes a point where the sorbed species desorb back into solution. When adsorption and desorption rates are equal, equilibrium has been achieved. The position of equilibrium is dependent upon the whole system and includes; the solute, the adsorbent, temperature and pH (Faust and Aly, 1987). The amount of solute adsorbed at equilibrium can increase if there is an increase in solute concentration.

Adsorption isotherms are a means of presenting the amount of solute adsorbed per unit of adsorbent, as a function of the equilibrium concentration in bulk solution (at a constant temperature).

Oxenford and Jykins Jr (1991) suggested that isotherms are used extensively to describe adsorption behaviour and to estimate the adsorption capacity of activated carbon throughout various processes, in removing organics from water.

Isotherms can be used in different ways to;

1) Select the most appropriate carbon.
2) Estimate its life within an adsorber.

3) Test the remaining adsorption capacity of a carbon in an adsorber.

There are a number models used for the presentation of adsorption data. These include; Langmuir's Adsorption Isotherm, Freundlich's Adsorption Isotherm, BET Adsorption Isotherm, and finally Henry's Law Linear Adsorption Isotherm. The Freundlich Isotherm is the most widely used mathematical model of an aqueous adsorption system. The Freundlich equation is described as an empirical mathematical expression that takes into account the heterogeneity of the adsorbent surface, the exponential distribution of sites, and their associated energies. The equation is presented as follows (Crittenden *et al*, 1987).

$$\frac{x}{m} = KC_e^{\frac{1}{n}} \qquad \textbf{(eqn 1.15)}$$

or

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \qquad \textbf{(eqn 1.16)}$$

Where x = the amount of solute adsorbed (mg), m = the mass of the adsorbent (g), C_e = the solute equilibrium concentration (mg/L), and K (mg/g) $(L/mg)^{1/n}$ and 1/n are constants of the system. x/m is sometimes referred to as the loading rate of a carbon (mg/g).

The constant K is related to the capacity of the adsorbent, for a particular adsorbate. 1/n is a function of the strength of adsorption. Referring to equation 1.15 it can be noted that for fixed values of K and C_e, the smaller the value of n, the more sensitive the adsorbent to the concentration. For fixed values of C_e and 1/n, the larger the K value, the greater the adsorption capacity.

If log x/m is plotted against log C_e a straight line can be observed. The line will have a slope of 1/n, where K is the intercept of log x/m at log C_e = 0 (Faust and Aly, 1987).

Most organic compounds have a 1/n value <1. Steeper slopes (where 1/n is close to 1) indicate high adsorptive capacity at high equilibrium concentrations. The adsorptive capacity is reduced dramatically at lower equilibrium concentrations covered by the isotherm. When 1/n is relatively low (1/n = <<1), the adsorptive capacity is only slightly reduced at lower equilibrium concentrations. As x/m (the loading capacity) is a function of the equilibrium constant, the higher the equilibrium constant, the higher the capacity for the adsorbent.

If $C_{in} - C_{eff}$ is substituted into the equation, the isotherm can be used to calculate the amount of activated carbon required to reduce the initial concentration to a predetermined final. Hence;

$$\log ((C_{in} - C_{eff})/ m) \cdot Vol = \log K + \frac{1}{n} \log C_e \qquad \textbf{(eqn 1.17)}$$

Where C_{in} = initial concentration of contaminant (mg/L), C_{eff} = required contaminant concentration (mg/L) and Vol. = volume (mg/L). Note that equation 1.10 applies to batch tests only.

1.6.2.5.2. MTBE and BTEX Equilibrium Studies.

Table 1.13 shows the Freundlich isothermal constants for BTEX compounds where K = (g/g) $(L/mg)^{1/n}$ .The BTEX compounds were added to F400 GAC and shaken for 2 days at 22°C (Faust and Aly, 1987).

	Single-Solute System		**Mixed-Solute System**	
	K	1/n	K	1/n
Benzene	36	0.48	8	0.60
Toluene	90	0.30	23	0.50
Ethylbenzene	100	0.40	65	0.30
o-Xylene	120	0.22	75	0.27

Table 1.13. Isothermal Constants for BTEX Compounds. Source: Faust and Aly, 1987.

From table 1.13 it can be seen that competitive adsorption plays a part in mixed solute systems as K is larger for the single solute systems and the 1/n value is closer to 1. When the 1/n value is low the adsorptive capacity is only slightly reduced at lower equilibrium concentrations.

Table 1.14 details Freundlich isothermal data for BTEX compounds, when the adsorbents used were the macroreticular resins Ambersorb 563, Ambersorb 572 and Ambersorb 600. Isothermal data was taken from a study carried out by Lin and Huang (1999) where K = (g/g) $(L/mg)^{1/n}$.

		Ambersorb 563	Ambersorb 572	Ambersorb 600
Benzene	K	100.6	68.7	38.2
	1/n	0.25	0.39	0.47
Toluene	K	87.2	86.6	24.2
	1/n	0.43	0.43	0.63
Ethylbenzene	K	56.9	201.8	110.5
	1/n	1.06	0.75	0.68
Xylene	K	52.1	79.3	133.1
	1/n	0.83	0.81	0.54

Table 1.14. Isothermal Data for Macroreticular Resins (Lin and Huang, 1999).

When considering tables 1.13 and 1.14 it can be observed that the 1/n values for benzene and toluene are lower for the resins, whilst for ethylbenzene and xylene they are lower for the F400 GAC. The values for K are higher for the macroreticular resins, suggesting better adsorption capacity.

Adsorption isotherms can provide an understanding of how a carbon may respond under the various conditions expected in water treatment works, although some degree of uncertainty must be accepted.

Although adsorption isotherms are useful for obtaining preliminary data concerning GAC adsorptive capacity, they do not yield sufficient data to develop design criteria for GAC treatment systems (Dyksen and Hess, 1982). The isotherms are determined in laboratory batch processes, whereas full-scale GAC treatment processes are continuous and dynamic. Prediction of the breakthrough point at field scale is difficult because isotherms are unable to account for background organic matter (BOM) and other uncharacterised compounds, which can interfere with the adsorption of certain compounds (Giffin and Davis, 1998).

1.6.2.6. Column Studies.

Isothermal batch tests can provide useful data on the difference between adsorbents and the magnitude of competitive adsorption. However, isotherm tests are static, equilibrium-based tests and hence have limitations on transposing the data into the operational and kinetic data needed to design full-scale adsorbers

(Shih *et al* 2003). Small-scale columns and pilot studies are necessary to develop design criteria. Small-scale tests are usually laboratory based, and along with isothermal and equilibrium data can be used to help predict the performance of adsorbents at full-scale.

The following terms are sometimes used when designing continuous adsorption processes;

1.6.2.6.1. Mass Transfer Zone (MTZ).

Figure 1.11 shows the concentration profile of an adsorbent moving through a fixed bed adsorption column (Crittenden, 1998).

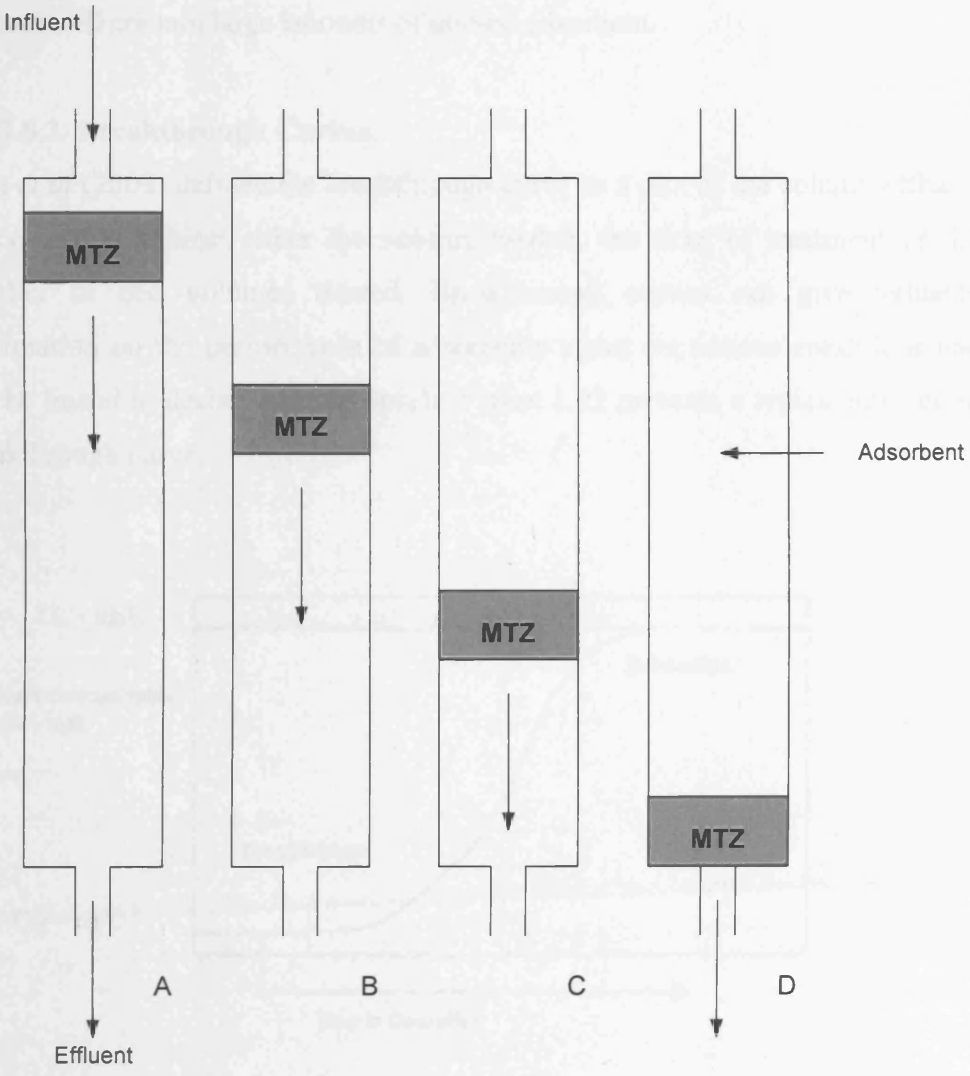


Figure 1.11. Movement of the MTZ through the Adsorption Column.

The transfer of the solute from solution to the adsorbent begins near the entrance of the column (A). Once saturated the zone in which adsorption is occurring (the mass transfer zone - MTZ) moves further down the column (B-C) and eventually reaches the bottom of the column (D). It can be noted that the adsorbent upstream of the MTZ has reached equilibrium and does not participate in any mass transfer. Downstream of the MTZ the adsorbent will have the capacity to adsorb the solute, but will not do so as adsorption is occurring above. Once the MTZ has reached the bottom of the column, breakthrough of the compound occurs and the column is taken off-line while the adsorbent is regenerated or replaced. If the progress of the MTZ through the column is too quick, then the column will contain large amounts of unused adsorbent.

1.6.2.6.2. Breakthrough Curves.

Shih *et al* (2003) defined the breakthrough curve as a plot of the column effluent concentration against either the volume treated, the time of treatment or the number of bed volumes treated. Breakthrough curves can give valuable information on the performance of adsorbents under continuous conditions and can be linked to desired effluent levels. Figure 1.12 presents a typical adsorption breakthrough curve.

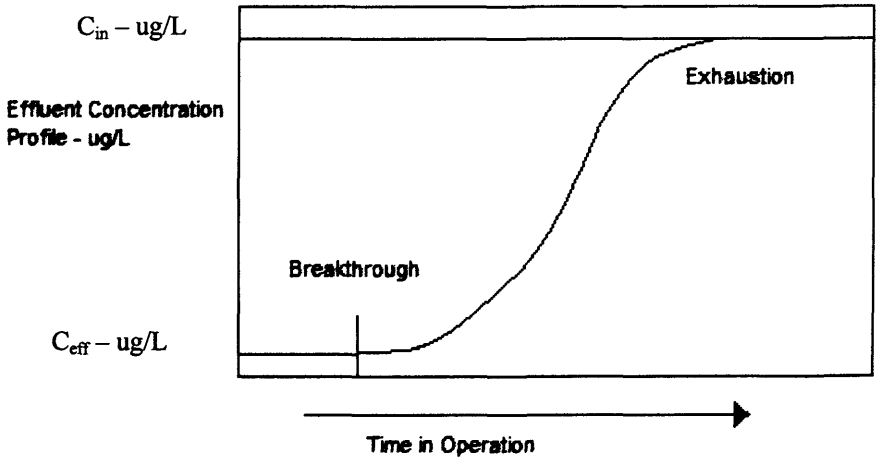


Figure 1.12. Typical Adsorption Breakthrough Curve.

Note that breakthrough occurs when the adsorbate is detected in the effluent (C_{eff} - μg/L). Exhaustion of the carbon occurs when C_{in} (μg/L) equals C_{eff} (μg/L). Adsorption occurs throughout the entire curve until exhaustion.

1.6.2.6.3. Empty Bed Contact Time (EBCT).

The contact time of GAC and water can be the most important factor in the design of a GAC adsorber and is widely used in the water industry. Contact time is commonly expressed as the empty bed contact time (EBCT), which is defined in equation 1.18.

$$EBCT = \frac{\text{Bed Volume}}{\text{Flow Rate}} \qquad \textbf{(eqn 1.18)}$$

The EBCT can also be used to scale-up small-scale adsorbers into full-scale adsorption units The usage rate of the adsorbent can sometimes be plotted against the EBCT to show information on carbon use at increasing EBCTs.

1.6.2.6.4. Rapid Small-Scale Column Tests (RSSCT).

Shih *et al* (2003) stated that the correct selection of a cost effective GAC and its associated operational parameters are vital for the operation of a full-scale GAC treatment plant.

Small-scale column tests use small GAC particles and column sizes in order to reduce the operation time compared to that of a pilot plant, hence dramatically reducing the cost. The GAC is usually crushed until it is an appropriate size for the column. Once added to the column it can have a bed depth of only a couple of centimetres. Studies have shown that carbon applied in this way has the same adsorptive capacity to that of the original carbon (Oxenford and Jykins Jr, 1991). RSSCTs have been shown to be reliable predictors of full-scale adsorber units, as breakthrough curves produced from RSSCT have been shown to be equivalent to those of a pilot-scale or full-scale column.

Lang *et al* (1993) suggested that the ratio between filter column diameter and media diameter should be greater than 50. This ratio was suggested in order to reduce the extent to which wall effects can alter the flow through a column. The porosity at the wall of a bed is greater than that in the prevailing body of the bed,

this can have adverse effect on the hydraulics of the bed and hence will not accurately reflect the behaviour of the adsorbate in the column.

The advantage in using small-scale columns include;

1) Assessment of both adsorption capacity and kinetics.
2) Low capital and operational costs.
3) The elimination of the need for numerical models.

One disadvantage in the use of small-scale columns is that if the water used within the experiment is not identical to that used in full-scale operations, they then cannot predict the impact of influences such as those caused by background organic matter (BOM).

BOM has been found to decrease the adsorptive capacity of a pilot column by up to 50%, compared to that of an RSSCT (Crittenden *et al,* 1991). It is for this reason that RSSCT's can only be used for preliminary design information. A pilot scale run will be needed to calibrate the RSSCT. The small scale rig can the be used to:

1) Evaluate certain design parameters such as EBCT, columns in series/ parallel etc.
2) Assess pre-treatment options such as coagulation/ ozonation etc.
3) Assess influent variation such as differing BOM concentration.

Crittenden *et al* (1991) stated that the similarities of the small-scale and large-scale adsorbers can be assured by properly selecting the particle size, hydraulic loading and empty bed contact time (EBCT) of the small-scale adsorber.

The RSSCT can be used to selectively screen different GAC media, prior to pilot testing.

1.6.2.7. Design of Full-Scale Adsorbers.

Adsorption is possible in both batch and continuous processes, both of which have been used in the water industry. There are many different configurations of continuous processes available. These include both fixed-beds and moving-beds. Fixed-bed processes are most commonly used in water treatment application.

Adsorption isotherms can be roughly used to estimate the GAC loading rate and bed life (Crittenden, 1998 and Faust and Aly, 1987). The bed life Z can be defined as;

$$Z = (q_e)_0 \times p / C_{in} - C_{eff} \qquad \textbf{(eqn 1.19)}$$

Where Z = bed life in L of water per L GAC, $(q_e)_0$ = mass adsorbed when C_{eff} = C_{in} (mg/g of GAC), p = apparent density of GAC (g/L), C_{in} = influent concentration (mg/L) and C_{eff} = average effluent concentration for entire column run (mg/L).

1.6.2.8. Competitive Adsorption.

Shih *et al* (2003) suggested that natural organic matter (NOM – a complex mixture of fulvic and humic acids, hydrophilic acids and carbohydrates) can cause significant reduction in the adsorptive capacity of GACs for target organics. NOM was found to impact the removal of specific organics in three ways;

- Reduction in the number of adsorption sites,
- Pore blockage and
- Irreversible adsorption of NOM to GAC adsorption sites which may permanently remove those sites from adsorption to trace organics.

The competitive effects of NOM between target compounds such as MTBE and other organic compounds such as BTEX can cause further reduction in the adsorptive capacity of GAC. This is because a greater percentage of the available adsorption sites become utilised by competitive compounds. The magnitude of the adsorptive effects in a multi-component system is complicated by factors such as the GAC type and the variety of competing species each having different adsorbabilities and concentrations.

Sorial *et al* (1993) wrote that in the case of mixtures, competitive adsorption is most likely to occur since the available surface area of the carbon will be occupied, to varying degrees, by the more adsorbable components. Competitive displacement of previously adsorbed compounds, such as MTBE, from those compounds more amenable to adsorption (e.g. BTEX) can occur. In these cases, the effluent concentration of MTBE may be greater than the influent concentration. The unique physical and chemical properties of MTBE will contribute to the competitive displacement of the compound from the GAC. These are driven by the fact that MTBE is more soluble than the BTEX compounds.

Munz *et al* (1990) stated that competitive adsorption in multisolute systems was a well known phenomenon that would need to be considered when designing GAC systems. It was suggested that every natural water source contains dissolved organic substances and that these were usually present in much higher concentrations than the trace organic contaminants of concern. Of the dissolved organic substances, humic compounds are thought to play a significant role in competitive adsorption.

The pre-treatment of water feeding a GAC column can have a significant effect on the activated carbon system. The removal of NOM by coagulation, sedimentation and filtration can reduce the amount of organics to be removed by the adsorption process, hence reducing the organic load on the carbon. It is worth noting that NOM will be much higher in surface waters than in groundwater systems.

The reactions of oxidative pre-treatment chemicals such as chlorine/ ozone/ chlorine dioxide and permanganate with GAC, or the presence of organic compounds in the aqueous solution (or on the surface of the carbon), can alter the adsorption performance.

Chen *et al* (1989) suggested that GAC capacity increased by approximately 20% when receiving ozonated water and that this was most likely due to the increase in biodegradability of the organics, as a result of the preoxidation.

Hooper *et al* (1996) studied the effect of optimising coagulation prior to GAC treatment. The study looked at the removal of NOM, TOC and disinfection by-products (DMPs). It was found that higher alum doses improved GAC performance, due to the removal of TOC from within the influent water. Since most water treatment works have coagulation facilities in place, this option could be implemented relatively easily.

The improvement in GAC performance after extensive coagulation was attributed to three factors (Hooper *et* al, 1996);

1) Lower influent TOC concentration to the GAC columns.
2) Lower influent pH.
3) An improvement in the adsorbable character of the NOM.

Research using batch isotherm tests has suggested that adsorption capacity increases with decreasing pH values for a number of water sources. This can be attributed to;

1) A decrease in the solubility of the organic compound.

2) A decrease in the size of the organic molecules.

3) Neutralisation of the GAC surface charge by hydrogen ion adsorption.

At high initial NOM levels the amount of carbon may not be sufficient to completely adsorb the most adsorbable compounds. These compounds effectively out-compete the less adsorbable compounds (such as MTBE). Through pre-treatment, lower NOM levels would mean that most of the strongly adsorbable fraction was removed, allowing the less adsorbable compounds to be adsorbed.

Increasing the alum dosages in the range examined by Hooper *et al* (1996) decreased the TOC concentration and pH (both of which are known to increase the adsorption capacity of carbon), lowering the run times by up to 2-3 times over conventional treatment.

1.6.3. AOPs.

The advanced oxidation process utilises hydroxyl free radicals (·OH) to initiate a reaction with organic chemicals within the water. This leads to the mineralisation of the pollutant, eventually forming carbon dioxide and water. AOP processes usually take place in a series of carefully controlled reaction chambers. The hydroxyl free radical typically attacks the organic species by removing a hydrogen atom or adding to the double bond of the unsaturated compound (Hernandez *et* al, 2002).

Commonly used advanced oxidation pathways in water treatment use UV/ Peroxide to produce the free radicals. Ozone can also be used to produce free radicals. The advanced oxidation process has been found to remove 99.9% of various contaminants found in water, including benzene and pesticides (Chang and Young, 2000).

All advanced oxidation techniques rely on hydroxyl free radicals (·OH) initiating a reaction with the organic compounds. One of the most efficient techniques for producing free radicals is the photodecomposition of hydrogen peroxide. Within the photodecomposition process detailed in equation 1.20, UV radiation cleaves the O-O bond within the hydrogen peroxide molecule to generate the free radicals. The free radicals are then free to oxidise other organic species, react

with other free radicals to reform hydrogen peroxide, or to initiate the chemical degradation of hydrogen peroxide in a chain reaction.

$$H_2O_2 + UV \rightarrow 2{\cdot}OH \qquad \textbf{(eqn 1.20)}$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + \cdot HO_2$$

$$\cdot HO_2 + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH$$

$$2{\cdot}HO_2 \rightarrow H_2O_2 + O_2$$

The free radicals are eventually consumed by reaction with the pollutant, inorganic compounds that may be present in the matrix and/ or the initial oxidiser itself.

Unlike the use of GAC or air-stripping which only transfers the contaminant from one phase to another, advanced oxidation can lead to the complete removal (degradation) of the chemical. The major disadvantage of advanced oxidation is the potential for the production of by-products that in some cases are more toxic than the original compound. Although the advanced oxidation process will eventually mineralise these compounds, the removal rates might be unfavourable. The formation of harmful by-products may also be dependent upon the characteristics of the water being treated. The presence of other organic species that are also susceptible to attack by free radicals can affect the degradation of the targeted contaminants. These species include carbonate, bicarbonate, humic substances and phosphate ions.

Speth and Swanson (2002) suggested that both effluent DOC and TOC concentrations were reduced from their initial concentrations within a contaminated groundwater, in a study on the AOP destruction of MTBE. This suggested that some organic carbon was destroyed by the AOP.

The primary design parameter for AOP systems is the electrical energy required for the destruction of the given contaminant.

1.7. Air-Stripping, Adsorption and AOP Studies.

The following section details air-stripping, adsorption and AOP studies in turn. The effectiveness, efficiency and capacity of each technique in the removal of BTEX and MTBE compounds from contaminated groundwater are presented.

1.7.1. MTBE and BTEX Air-Stripping Studies.

Volatile compounds such as BTEX compounds are known to be amenable to air-stripping due to their high volatilities. Hung *et al* (2002) stated that although MTBE has a relatively high vapour pressure compared to that of benzene (P^{o}_{v} = 32.4kPa compared to 10.1 kPa respectively - i.e. roughly three times as volatile as benzene), this is offset by the fact that MTBE prefers to remain in water. Therefore MTBE is characterised by having a low Henry's Law Constant. In turn this means that a much greater volume of air would be required during air-stripping to remove the compound (compared to the removal of BTEX compounds).

Gerbasi and Memoli (1994) stated that there would be an increase in the operating costs of an air-stripping tower when removing MTBE, as deeper beds and higher air-to-water ratios (>100:1) would be needed.

Shih *et al* (2003) stated that air-stripping may not be cost effective in removing MTBE from water, as over 6 times the air-to-water ratios may be required (compared to other petroleum compounds).

The American Petroleum Institute (API) evaluated the performance of MTBE removal during air-stripping on a number of sites within the US. They found that MTBE removal efficiencies ranged from 55% to 100% (with a median value of 91%), for 15 of the 57 sties monitored (Burgess *et al*, 1998).

Safarzadeh-Amiri (2001) suggested that the implementation of air-stripping technology would require air-to-water ratios >200/1 to provide a MTBE removal rate of 95%.

Sutherland *et al* (2004) conducted air-stripping experiments for five different groundwater sites with varying MTBE concentrations. Influent flow rates were 15 L/min with air-to-water ratios of 75:1, 100:1 and 150:1. General observations made by Sutherland *et al* (2004) were that the mass transfer coefficients determined from the experimental data were low for each groundwater, at each flow rate tested. This was attributed to the low Henry's Law Constant and high

solubility of MTBE. For each groundwater, greater air-to-water ratios correlated with increased mass transfer. It should be noted that no significant correlation was observed between the mass transfer coefficient at a given air-to-water ratio and chemical oxygen demand (COD), influent MTBE and BTEX concentration or alkalinity. Sutherland *et al* (2004) suggested that fouling of the packing material could occur in groundwaters that contain significant ferrous iron, high hardness (which leads to carbonate scaling as carbon dioxide is stripped) or nutrients (which may need to biofouling). Using the appropriate derived mass transfer coefficients and required removal efficiencies (80% and 99.5%), Sutherland *et al* (2004) calculated the required tower height for each groundwater application. Because of the low mass transfer coefficient, tower heights (especially for lower air-to-water ratios) were sometimes found to be uneconomical (up to 24m in height). The results showed that required packing heights for an air-to-water ratio of 75:1 were 1.5 – 3.0 times greater than that for an air-to-water ratio of 150:1.

Stover and Kincannon (1983) studied the removal of VOC's (benzene, toluene and ethylbenzene) using a laboratory scale air-stripping column. The results of the study are summarised in table 1.15.

	Compound	Air-to-water Ratio	Influent Conc. (µg/L)	Effluent Conc. (µg/L)	Removal Efficiency (%)
Run 1	Benzene	53	68.8	59.7	13
	Toluene		92.0	30.0	67
	Ethylbenzene		23.5	0.053	100
Run 2	Benzene	26	68.8	68.8	0
	Toluene		92.0	23.3	75
	Ethylbenzene		23.5	-	-
Run 3	Benzene	53	68.8	39.5	43
	Toluene		92.0	19.0	79
	Ethylbenzene		23.5	0.5	98
Run 4	Benzene	107	68.8	-	-
	Toluene		92.0	17.1	81
	Ethylbenzene		23.5	0.6	97
Run 5	Benzene	396	68.8	36.0	48
	Toluene		92.0	6.6	93
	Ethylbenzene		23.5	-	-
Run 6	Benzene	9	68.8	68.8	0
	Toluene		92.0	44.8	51
	Ethylbenzene		23.5	1.0	96

Table 1.15. Air-Stripping Results from Laboratory Scale Column Experiments (Stover and Kincannon, 1983).

It can be seen from the study by Stover and Kincannon (1983) that ethylbenzene was most amenable to removal by air-stripping, followed by toluene and finally benzene. This is consistent with the physical and chemical properties of the respective compounds, with an increase in water solubility and decrease in molecular weight in the order ethylbenzene – toluene – benzene. It can be noted that the removal efficiency of ethylbenzene is significantly better than that of benzene.

1.7.2. MTBE and BTEX Adsorption Studies.

Most of the recent literature detailed within this section on the adsorption of fuel oil compounds have concentrated on MTBE. However, within most of the MTBE studies, BTEX compound have also been included to study the effects of competitive adsorption.

MTBE is known to be poorly sorbed onto carbon substrates; hence the compound is less amenable to adsorption by GAC. The lower tendency for MTBE to be retained by organic carbon is reflected in its octanol-water partition coefficient (K_{OW}), where the K_{OW} for MTBE has been determined to be two orders of magnitude less than that of benzene.

The USEPA suggested that GAC is approximately 1/3 – 1/8 as effective in removing MTBE as it is benzene from contaminated groundwater (USEPA, 1998). The American Petroleum Institute (API) reports an adsorption capacity of 0.004g MTBE per 1.0g GAC (0.004 g/g). This is compared to 0.3g BTEX per 1.0g GAC (0.3 g/g) (Burgess *et al,* 1998).

Sutherland *et al* (2004) investigated the removal of MTBE from contaminated groundwater sources using F400 and F600 GAC. In some of the groundwater sources, BTEX compounds were also present. Table 1.16 summarises the findings of the study.

	GAC	Influent Conc. MTBE (mg/L)	Influent Conc. BTEX (mg/L)	Ultimate GAC Capacity (mg/g)
A	F400	5.03	<0.0005	9.3
	F600	5.31	<0.0005	20
B	F400	0.963	<0.0005	2.52
	F600	1.26	<0.0005	5.52
C	F400	0.023	1.1	0.11
	F600	0.029	3.6	0.17
D	F400	0.198	0.052	0.86
	F600	0.224	0.17	1.9
E	F400	0.033	0.011	0.25
	F600	0.039	0.018	0.46

Table 1.16. Summary of MTBE Adsorption Study (Sutherland *et al*, 2004).

Sutherland *et al*, 2004 made several specific observations from the study;

- For all groundwaters, F600 carbon had significantly greater breakthrough and ultimate capacities for MTBE than F400 by a factor of from 1.5 – 2 times
- The results indicated that there was a strong correlation between influent MTBE concentration and capacity on both F400 and F600 GAC
- The adsorption data showed that BTEX compounds were preferentially retained within the carbon compared with MTBE. The result of the preferential adsorption of BTEX was to displace the MTBE from the carbon. This was expected based on relative water solubility, K_{OW} values and Freundlich coefficients
- Overall the data suggested that GAC adsorption capacities for MTBE is enhanced in situations where the influent MTBE concentration is high and competitive adsorption effects are low.

Davis and Powers (2000) studied the adsorptive capacity of a number of different alternative adsorbents in removing MTBE and gasoline contaminants from groundwater. The overall objective of the study was to identify sorbents other than GAC for the effective removal of MTBE from groundwater. Sorbents included; synthetic carbonaceous resins, porous graphitic carbon, C_{18} silicas and acrylic resins. Activated carbon (F400) was also tested for comparison purposes. The results of the adsorptive batch tests are summarised in table 1.17.

	Sorption Capacity (mg/g)
F400	3.1
Ambersorb 563	16.2
Ambersorb 572	13.8
Hypercarb	6.5
Polysorb MP-1	0.8

Table 1.17. Sorption Capacity of Various Alternative Adsorbents.

It can be observed from the study by Davis and Powers (2000) that the sorption capacity of F400 was similar to that seen in the study by Sutherland *et al* (2004) (when BTEX was not present in the influent solution).

Isothermal data from the study by Davis and Powers (2000) showed that the porous graphitic carbon and the carbonaceous resins both had a greater capacity for the removal of MTBE than F400. However, preparation of the graphitic carbon made the material unsuitable for drinking water purposes.

At an equilibrium concentration of 1 mg/L and when no other contaminants were present, Ambersorb 563 was found to have five times the adsorptive capacity of F400 GAC in removing MTBE. When m-xylene was present in solution, this increased to six times the capacity of F400. This suggests that alternative adsorbents would be the media of choice in a multi-solute influent water.

When m-xylene was added to the batch tests (used as a representative BTEX contaminant), the compound was preferentially adsorbed with respect to MTBE. The extent of the interaction varied between adsorbents. Although the reduction in the Ambersorb 572 capacity was the least amongst the three carbonaceous resins, Ambersorb 563 still had an adsorptive capacity 50% higher than Ambersorb 572.

The use of resins has also been investigated for the removal of BTEX compounds. Lin and Huang (1999) studied the adsorption of BTEX compounds using the following macroreticular resins; Ambersorb 563, 572 and 600. BTEX adsorption by these resins (both in batch and continuous processes) was found to be highly efficient. However, Lin and Huang (1999) suggested that little was known about the use of these compounds in the water industry and indeed for the removal of hydrocarbons from groundwater.

Shih *et al* (2003) evaluated the use of different GAC types on the removal of MTBE from both a groundwater source and a surface water source using rapid small-scale column tests (RSSCT). The objective of the study was to validate and optimise GAC performance in removing MTBE in the presence of competitors such was benzene, toluene and *p*-xylene (BTX), natural organic matter (NOM) and breakdown products of MTBE (e.g. TBA). Two types of coconut-based GACs were used within the study; PCB (produced by Calgon Carbon) and CC602 (produced by US Filter). These specific carbons were recommended by the respective manufacturers at the time of the study.

Carbon capacities were made based upon their performance in removing MTBE from a surface water lake and are detailed in table 1.18 where;

- Influent concentration of MTBE = 20 μg/L,
- Influent concentration of Benzene = 108 μg/L,
- Influent concentration of p-xylene = 97 μg/L and
- Influent concentration of TBA = 100 μg/L.

	EBCT (min)	GAC capacity at 50% breakthrough (mg/g)	GAC capacity at saturation (mg/g)
CC – 602	10	0.072	0.110
PCB	10	0.114	0.142
CC – 602	20	0.136	0.186
PCB	20	0.168	0.217

Table 1.18. Adsorptive Capacity for Various GACs for MTBE.

Data from table 1.18 suggests that the breakthrough behaviour of the carbons were similar. However, when Shih *et al* (2003) analysed the respective breakthrough curves, the curve for CC-602 GAC was characterised by a steep rise which levelled of at ~70% breakthrough (i.e. rapid partial breakthrough followed by an extensive plateau region), while the breakthrough curves for the PCB GAC were characterised by a more gradual and constant breakthrough behaviour. For this reason the PBC GAC was considered superior since it demonstrated better performance in terms of adsorption kinetics and adsorption capacity over the most useful life of the carbon.

The study found that GAC performance was greatly reduced in the presence of total organic carbon (TOC), especially when testing surface waters containing medium concentrations of TOC (compared to groundwater which have low TOC concentrations). The competitive effect of BTX compounds was found to reduce the GAC usage rate by up to 30% (approximately), where a carbon with a lower usage rate produces a longer time to component breakthrough and hence time to regeneration.

As a low cost alternative to GAC, Daifullah and Girgis (2002) studied the adsorptive capacity of a number of botanical activated carbon precursors in the removal of BTEX compounds from solution. These included; date pips (DP), cotton stalks (CS), peach stones, almond shells (ALS) and olive stones. These produced activated carbons with highly developed pore structures.

The adsorptive capacities of each respective activated carbon are detailed in table 1.19. For comparison purposes, PAC (Prolabo) was also tested.

	Benzene Capacity (mg/g)	Toluene Capacity (mg/g)	Ethylbenzene Capacity (mg/g)	Xylene Capacity (mg/g)	Total BTEX Capacity (mg/g)
DP	8.8	5.0	5.6	6.2	25.6
CS	3.0	6.7	8.7	9.3	27.7
PS	3.0	6.5	8.3	8.7	26.5
ALS	1.3	5.0	6.5	7.4	20.2
OS	8.3	5.8	6.6	7.2	27.9
PAC	7.9	9.2	9.2	9.9	36.3

Table 1.19. Adsorptive Capacities of Various Botanical based Activated Carbons.

Daifullah and Girgis (2002) observed that in terms of the order of removal of each compound; B < T < E < X. This is consistent with the relative decrease in water solubility and increased molecular weight observed within the BTEX compounds.

Three carbons showed potential for BTEX adsorbents; PS, ALS and CS. OS and DP showed relatively lower feasibility in the removal of BTEX compounds from solution.

1.7.3. MTBE and BTEX AOP Studies.

MTBE has been found to be resistant to oxidation using common water treatment operations such as exposure of the water to UV light at 254nm. However, it is possible to use advanced oxidation for the remediation of MTBE in other ways.

As with the advanced oxidation of other organic species such as BTEX compounds, hydroxyl free radicals are used to attack the MTBE. Chang and Young (2000) suggested the following pathway for MTBE destruction;

- $OH\cdot + (CH_3)_3COCH_3 \rightarrow H_2O + (CH_3)_3COCH_2\cdot$
- $(CH_3)_3COCH_2\cdot + O_2 \rightarrow (CH_3)_3COCH_2OO\cdot$
- $(CH_3)_3COCH_2OO\cdot + (CH_3)_3COCH_3 \rightarrow (CH_3)_3COCH_2OOH + (CH_3)_3COCH_2$
- $(CH_3)_3COCH_2OOH \rightarrow (CH_3)_3COCHO + H_2O$ **(eqn 1.21)**

Chang and Young (2000) suggested that nearly complete removal of MTBE (99.9%) could be achieved using an ozone/ peroxide (UV/H_2O_2) treatment process. However, it was observed that as the concentration of MTBE decreased, the concentration of the by-product tertiary-butyl formate (TBF) increased. A study conducted by Safarzadeh-Amiri (2001) suggested that the effectiveness of the UV/H_2O_2 process for the degradation of MTBE was affected by the influent concentration of MTBE and by the presence of BTEX compounds.

Other AOPs have been applied to the removal of MTBE. These include; oxidation using ozone and oxidation using UV-ozone (Graham *et al*, 2004). Results from the studies carried out by Graham *et al*, 2004 showed that oxidation using UV-ozone was twice as effective in the removal of MTBE as oxidation using ozone alone. This was expressed graphically when the slope of the natural logarithm of the fraction of MTBE remaining was plotted against exposure time. The studies carried out by Graham *et al*, 2004 represented an overall rate constant of 0.0619 s^{-1} for ozonation alone and 0.128 s^{-1} for UV-ozonation. Based upon an influent concentration of 1200µg/L, the removal efficiencies for ozone AOP was 97.5% whilst the removal efficiency for UV-ozone AOP was 99.95%. However, as with other AOPs a number of by-products were produced which included; TBF, methyl acetate, butane, acetone and acetaldehyde.

Safarzadeh-Amiri (2001) studied the removal of MTBE using Ozone/ Peroxide (O_3/H_2O_2) treatment. The study suggested that the rate of oxidation of MTBE

was limited by the mass transfer of ozone and increased with ozone gas flow rate. The first order rate constant (for MTBE concentrations above 10 mg/l) followed a first order reaction rate and varied between 0.002 – 0.005 s^{-1}. Safarzadeh-Amiri (2001) suggested that the remediation of MTBE contaminated groundwater by O_3/H_2O_2 treatment was more efficient and less costly than the UV/H_2O_2 treatment process. However, note that the reaction rates were more favourable for the UV-ozone system (Graham *et al*, 2004) than in the O_3/H_2O_2 system (Safarzadeh-Amiri, 2001).

Within relevant literature there are conflicting ideas on whether advanced oxidation is a viable treatment option for the removal of MTBE.

Mitani *et al* (2002) suggested that advanced oxidation was a viable treatment option using ozone and ozone/ hydrogen peroxide in water. It was suggested that although air-stripping and GAC cost less to install and run, advanced oxidation had the advantage of not requiring an additional treatment step for the disposal of the pollutant. However, harmful by-products such as *t*-Butyl-formate (TBF) and *t*- Butyl-alcohol (TBA) were formed by the incomplete oxidation of MTBE during their experiments. TBF and TBA may pose a greater risk than health MTBE itself.

Shih *et al* (2003) suggested that although advanced oxidation could be used in the removal of MTBE from water, harmful by-products such as bromate could be produced, and hence would require additional removal before the water is distributed.

Burbano *et al* (2003) studied the chemical destruction of MTBE using Fenton's Reagent (FR). It was suggested that FR had been used successfully in the treatment of low concentrations of MTBE (1-2 mg/L) in water. Under certain reaction conditions, up to 99.9% of transformation was achieved, but did not yield complete MTBE mineralisation. TBA, TBF, methyl acetate and acetone were identified as process by -products. Equation 1.22 presents the FR catalytic decomposition of hydrogen peroxide by a transition metal such as ferrous iron (Fe^{2+}). Hydrogen peroxide is decomposed to the hydroxyl radical and hydroxyl ion while the ferrous iron is transformed to the ferric iron (Burbano *et al*, 2003).

- $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + OH^-$ **(eqn 1.22)**

A recent report by Hung *et al* (2002) suggested that MTBE was efficiently removed from groundwater using ultrasonic irradiation in the presence of ozone,

in a sonolytic process. Three different types of reactors were used, with the vibrating-plate reactor providing the most efficient removal (run at 358 kHz). The high removal rate of MTBE using ultrasound and ozone was attributed to the effective production of the hydroxyl radical, even at high alkalinity. Hydroxyl radicals were found to oxidise carbonate, which formed carbonate radicals. These radicals then attacked the MTBE via hydrogen extraction.

Literature sometimes warns against using advanced oxidation in the removal of MTBE, as problems can occur during the advanced oxidation process. MTBE is regarded a relatively unreactive compound. AOPs have the added complication of the oxidation of other compounds present in water. Harmful by-products due to incomplete oxygenation can lead to the formation of aldehydes, ketones, alcohols and bromate (e.g. Graham *et al*, 2004 and Mitani *et al* 2002).

1.8. Literature Review Summary.

Section 1.8 of Chapter 1 summarises the findings of the literature review in order to define the overall aims of the fuel oil project.

Initially the study presented the world-wide problem of the fuel oil contamination of groundwater in terms of; groundwater as a drinking water source, sources of fuel oil contamination, the effect of MTBE and BTEX compounds on the quality of groundwater, drinking water standards and the health effects of MTBE and BTEX compounds. Case studies were presented in order to provide an indication of the likely levels of MTBE and BTEX compounds in contaminated groundwaters.

Section 1.2 of Chapter 1 introduced groundwater movement and geochemistry.

Section 1.3 of the literature review detailed the chemical breakdown of fuels, as well as the chemical and physical properties of compounds within fuel. In particular Section 1.3 detailed the chemical and physical properties of MTBE and BTEX compounds. These compounds were identified throughout the initial stages of the literature review as being the compounds most likely to reach the groundwater after a fuel oil spillage and also those most likely to be transported downstream of the contaminant source within the aquifer.

Selective migration of fuel oil compounds throughout an aquifer is namely due to the relatively high solubility of BTEX compounds and the high solubility of MTBE. Table 1.20 compares the solubility of MTBE and BTEX compounds. Landmeyer *et al* (1998) suggested a chromatographic separation of MTBE with respect to BTEX compounds within groundwater aquifers, as MTBE was detected in boreholes downstream of a contaminant release before the BTEX compounds.

Compound	Solubility (mg/L)
Benzene	1750
Toluene	515
Ethylbenzene	152
M-Xylene	158
P-Xylene	156
O-Xylene	175
MTBE	48000

Table 1.20. Comparison of MTBE and BTEX Solubility. Source: Burgess et al, 1998, Perry and Green, 1984.

It was noted in Section 1.3.5.1 that once a petroleum contamination has occurred, the fuel will partition into three phases;

- Dissolved phase
- Liquid phase
- Gaseous phase.

A fraction of the mixture will dissolve into the soil moisture and groundwater, a liquid fraction will remain in the soil voids in its pure form (NAPLs) and a gaseous fraction of the fuel will occupy the air spaces within the soil pores.

The soluble components of fuel in contact with the water table (e.g. MTBE and BTEX), slowly dissolve and can lead to the formation of a contamination plume moving downstream of the contaminated area. The most soluble of these compounds (including MTBE) will form the leading edge of the contamination plume.

The USEPA have classified BTEX compounds as 'priority' compounds (Lin and Huang, 1999). Priority compounds are those regarded by the regulators to be of a greatest threat to both the environment and to human health. In particular, the USEPA regard benzene as a contaminant of concern within fuels because of its relatively high solubility and its known carcinogenicity.

Based on current toxicological data, Hartley et al, 1999 suggested a maximum drinking water limit of 100μg/L, however, the US state of California recently set the maximum contaminant level for MTBE as 5.0μg/L (Keller *et al*, 2000). This more conservative remedial target of 5.0μg/L was adopted throughout the experimental phase of the study. Currently there are no current WHO guidelines for MTBE.

Currently, there are different (world-wide) views and regulations with respect to the level of benzene and MTBE within drinking water. Although the UK has recently adopted a drinking water standard of 1.0μg/L for benzene, there are no standards for MTBE (or the remainder of the BTEX compounds). The 1.0μg/L value for benzene forms one of the most conservative drinking water standards in the world and was therefore adopted as the remedial target throughout the experimental phase of the present study.

Burgess *et al* (1998) stated that even though MTBE is thought to have a low toxicity, its presence in groundwater in concentrations above a few milligrams per litre is a serious situation at public water supply (PWS) boreholes and would demand remedial action on its own account.

Remediation Methods.

Pruden *et al* (2003) suggested that whilst the health effects of MTBE were still under scrutiny, there was a need to develop and optimise technologies for removing MTBE from groundwater, especially when downstream drinking water resources were of a concern. It was also suggested by Pruden *et al* (2003) that near the source of the plume, special consideration should be given to BTEX compounds.

In-situ methods remediation methods will always need to be implemented in any fuel oil contamination event. In addition to this, if the correct local hydrological and geochemical conditions exist, remediation strategies will need to be implemented at PWS boreholes to safeguard the quality of the drinking water.

The USEPA (1998) stated that pump and treat methods may be the preferred remediation technique for the removal of MTBE from groundwater. This is because MTBE is poorly sorbed by the soil and quickly finds its way into the groundwater.

The USEPA suggested that because MTBE behaves differently in soil and water than other petroleum constituents such as BTEX compounds that the remediation method employed after a contamination issue will be different if MTBE is present at a site (USEPA, 1998).

It is apparent from a review of the relevant literature that the three most common post-abstraction remediation technologies employed to clean up contaminated aquifers are;

- Adsorption, with GAC being the most commonly adsorbent,
- Air-stripping
- Advanced oxidation processes (AOPs).

A review of the literature presented conflicting opinions on the suitability, efficiency and effectiveness of air-stripping, adsorption and AOPs in the remediation of MTBE and BTEX compounds. Generally it was suggested that BTEX compounds were amenable to processes such as air-stripping and adsorption, whilst MTBE was generally not.

The literature review suggested that GAC adsorption and air-stripping are not only tried and tested technologies in municipal water treatment, but can also be used in the removal of VOCs (including BTEX) from contaminated groundwater. However, it was suggested that the technologies were not as good at removing MTBE from contaminated groundwater. Holden and Tunstall-Pedoe (1998) suggested that air-stripping was effective at removing most organic contaminants including BTEX compounds, but treatment of MTBE proved difficult and expensive because of the high air-to-water ratios that needed to be employed.

Giffin and Davis (1998) stated that GAC was a proven technology for the removal of BTEX compounds from contaminated groundwater. However, less is understood about the competitive effects between BTEX and MTBE compounds.

Keller *et al* (2000) suggested that air-stripping would be the lowest cost technology for the removal of MTBE at high flow rates (2.3-23m^3/hr) if no air treatment was required.

Note that air-stripping followed by a GAC adsorption polishing step has been suggested as a potential remediaton option for the removal of MTBE and BTEX compounds throughout literature (Davis and Powers, 2000, Munz *et al*, 1990).

Generally it can be considered that adsorption and air-stripping transfer contaminants from one phase to another, whilst AOPs leads to complete destruction of compounds but can lead to production of harmful by-products.

The majority of the literature suggested that AOP technology was able to achieve high BTEX and MTBE removal efficiencies (in some cases >99%). Shih *et al* (2003) suggested that UV/H_2O_2 treatment could be quite effective in the removal of MTBE from drinking water. It was suggested that an advantage of using advanced oxidation over air-stripping or GAC adsorption was that if performed

correctly, advanced oxidation would ensure that the contaminant is removed completely from the solution forming harmless by-products.

However, one major disadvantage of AOPs is that by-products are formed during the oxidation process, some of which can be more harmful than the starting compound itself. These by-products then present further problems in drinking water treatment. Hernandez *et al* (2002) suggested that although chemical oxidation was a well established method used in municipal water treatment, the technique still lacks a proven record for the removal of organic pollutants from water.

Keller *et al* (2000) suggested that the use of advanced oxidation processes (using ozone or ozone/ hydrogen peroxide) was in all cases more expensive than GAC and air-stripping. In their experiments, Keller *et al* (2000) used a series of different flow rates and influent concentrations to cover a range from high flow rate/ low concentration typical of surface waters, to low flow rate/ high concentrations typical of groundwater contamination.

Given that literature suggested that harmful by-products are formed throughout the AOP process, it was decided that GAC and air-stripping would be examined as suitable technologies for the treatment of drinking water throughout the experimental phase.

CHAPTER 2: AIMS AND OBJECTIVES.

Chapter 2 presents the aims and objectives of the present study, with respect to the experimental phase and desired outcome of the project. The aims and objectives were derived from a review of the current literature (Chapter 1), notably the literature review summary (Section 1.8 of Chapter 1).

2.1. Aims and Objectives.

The aims and objectives are presented below;

- It is an aim to provide an indication of an optimised remediation strategy for the simultaneous removal of MTBE and BTEX, utilising air-stripping and GAC columns in series. The air-stripper will be optimised to remove the bulk of the contamination and the adsorption column implemented as a polishing step.
- It is the aim of the fuel oil project to implement the most stringent world-wide remedial targets. For benzene this will be 1µg/L and for MTBE this will be 5µg/L.
- Literature suggested that it was possible that MTBE and BTEX compounds could be detected in groundwater at PWS boreholes after contamination events upstream. Literature cited many examples of MTBE and BTEX removal studies, however, the studies were generally applied to MTBE and BTEX removal separately. The present study will aim to provide an optimised remediation strategy for an MTBE – BTEX influent mixture simultaneously.
- Throughout literature, air-stripping studies utilised random packing for the removal of MTBE and BTEX compounds. Literature did not suggest that stainless steel structured packing had been implemented in groundwater remediation applications. Given the higher theoretical removal efficiency of stainless steel structured packing, the fuel oil project aims to provide an indication of the removal capacity of the structured packing material in a groundwater application.
- F400 and F600 GAC will be utilised as adsorbents throughout the experimental phase, as they are accepted world-wide throughout the water industry. Although literature suggested that alternative adsorbents have higher adsorption capacities of MTBE and BTEX than GAC, in most cases

alternative adsorbents still need regulatory approval for water treatment applications.

- F600 carbon was cited within literature as being a new product specifically aimed at MTBE removal from groundwater applications. F600 studies cited within literature were generally applied to MTBE removal only. An aim of this study is to provide an indication of the removal efficiency of F600 in removing MTBE and BTEX compounds simultaneously and compare it to that of F400. F400 carbon has been extensively cited within literature as a GAC suitable for general groundwater remediation applications.
- It is an aim of the fuel oil project to provide an indication of the role and magnitude that competitive adsorption plays in the remediation process. Adsorption of MTBE with other soluble aqueous fuel oil compounds (in this case BTEX) was thought to be more relevant than single –solute adsorption, since MTBE can occur within fuels alongside BTEX components and has been detected in PWS boreholes simultaneously.
- It is an aim of the fuel oil project to recommend areas of further investigation with respect to the optimised removal of MTBE and BTEX compounds simultaneously from contaminated groundwater.

2.2. Contaminant Levels Employed throughout the Study.

Throughout the literature review it was evident that many studies have been conducted with respect to the removal of MTBE and BTEX compounds from contaminated groundwater. However, in general BTEX and MTBE compounds would not be included in the same study. Although it is entirely feasible that BTEX and MTBE compounds could be detected in a groundwater drinking source separately, literature highlighted occasions when both MTBE and BTEX compounds would be detected in drinking water sources. For example Landmeyer *et al* (1998) suggested a chromatographic separation of MTBE with respect to BTEX compounds within groundwater aquifers. MTBE was found to breakthrough in boreholes downstream of a contaminant release initially, followed later by the detection of BTEX compounds. Given the chemical and physical properties of BTEX compounds, the migration of the contaminants downstream of the contaminant source cannot be ruled out. As highlighted in the case studies presented in Section 1.1.7 of Chapter 1, if the spillage

is close by, MTBE and BTEX will be detected at the borehole at approximately the same time.

The literature review suggested that if the MTBE concentration at a particular site was low enough that it is not of a significant environmental concern, then the remediation technique should concentrate on the removal of other compounds (such as BTEX). However if there are significant concentrations of MTBE, then MTBE would be the driving force behind the remediation technique. Rong (2001) suggested that the current state of knowledge on MTBE did not provide an accurate model of the movement of MTBE within groundwater, or the removal efficiencies associated with the best available treatment technologies. For this reason it was decided that BTEX and MTBE would be studied simultaneously throughout the experimental phase of the project, with the emphasis on process optimisation using stringent remedial targets.

Throughout literature, references are made to the concentrations of MTBE and BTEX compounds found within contaminated groundwater. These figures are usually expressed in case studies and are then transposed into full-scale or laboratory-scale remediation trials.

Contaminant levels tested throughout the present study were based upon some of these US based studies, as well as case studies from the UK. The case studies presented from the UK are likely to be more indicative of contaminant levels within Europe.

Keller *et al* (2000) suggested two general cases for the MTBE contamination of groundwater beneath LUSTS;

- Low MTBE concentrations (30 - 100µg/L) at high flow rates
- High MTBE concentrations (100 - 5000µg/L) at low flow rates.

Shih *et al* (2003) suggested that 20 µg/L was representative of an MTBE contaminated groundwater within the US.

Case Study 1 (Chapter 1.1.7) referred to the levels of MTBE and BTEX in a UK contaminated aquifer. Initial MTBE concentrations ranged from 0.1 – 32 µg/L. Case Study 2 also referred to the concentrations of MTBE and BTEX within a UK contaminated aquifer. Initial benzene concentrations ranged from 4.7µg/L - 234µg/L, with a maximum initial MTBE concentration of 25.5µg/L. Note that the levels experienced in both the UK case studies were similar to those proposed by Shih *et al* (2003).

Given the experimental time constraints, table 2.1 details the contaminant levels to be investigated throughout the experimental phase of the present study and the rational behind the decision.

	Upper Limit (µg/L)	**Rational**	**Lower Limit (µg/L)**	**Rational**
BTEX	100	Medium levels expressed in contaminated UK/ European groundwaters.	40	To compare the effectiveness of the remediation technique at lower BTEX influent concentrations.
MTBE	40	Levels similar to those expressed in UK and US case studies throughout literature.	5	To test the removal efficiency of BTEX with a minimal MTBE influent concentration.

Table 2.1. Rational behind Contaminant Levels.

Note that the concentration of BTEX refers to the level of each individual compound in the BTEX group. That is a total concentration of 600µg/L including all Xylene compounds (M-P-X-Xylene).

CHAPTER 3: MATERIALS AND METHODOLOGY.

The aim of the materials and methodology chapter is to present the design and evolution of the apparatus used within the experimental phase of the study and to detail how the apparatus was used to satisfy the project aims.

Two types of apparatus were used during the experimental period; the RSSCT and the pilot-plant. Although the experimental phase of the project focused on the pilot-plant - the design, use and experimental method relating to both the pilot-plant and the RSSCT will be looked at in detail in this chapter.

3.1. RSSCT Materials and Methodology.

The following section details the materials and method with respect to the RSSCT experimental work-plan. Technical problems were experienced with the RSSCT experimental plan and are detailed at the end of this chapter (3.4).

Both an initial RSSCT procedure and a revised RSSCT design and procedure are presented within this chapter. Due to the technical problems experienced with the RSSCT, the results of the RSSCT tests are presented in Appendix B.

3.1.1. Initial RSSCT Rig Design and Procedure.

Figure 3.1 presents the initial RSSCT design.

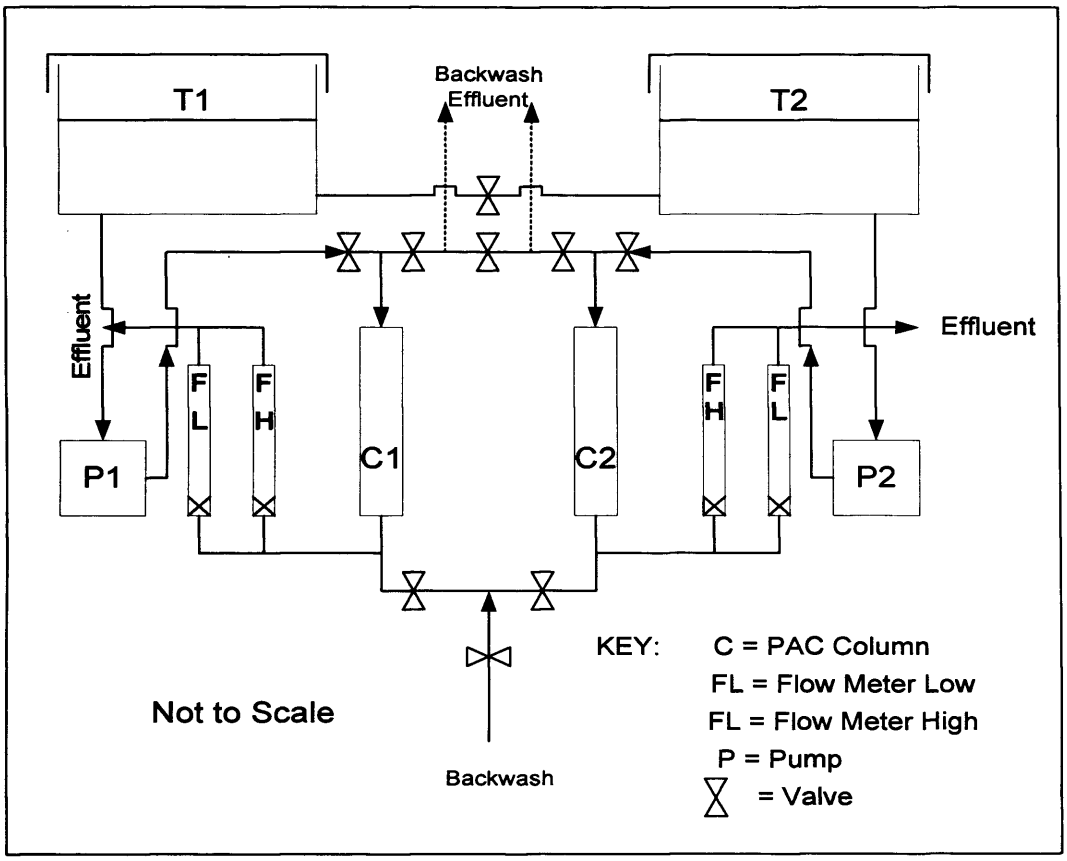


Figure 3.1. Initial RSSCT Design.

RSSCT Method of Operation.

The RSSCT comprised of two polypropylene feed tanks (80L x 2), two steel columns (100mm x 10mm), two Watson Marlow peristaltic pumps and associated steel piping/ valves (internal diameter 5mm). The RSSCT unit was mounted within a self-contained wooden frame.

The RSSCT design allowed experiments to be run using one of the adsorption columns. If required, the design of the RSSCT also allowed two experiments to be carried out simultaneously, using both adsorption columns. Tanks 1 and 2 were used to store the feed water dosed with the appropriate fuel. Peristaltic pumps 1 and 2 delivered influent water at pressure from the dosage tanks to the adsorption columns. Flow rates were controlled by two flow meters per column (one high and one low). Note that only the low flow meter was used throughout the RSSCT experimental work. Aqueous samples from the RSSCT could be taken from the dosage tanks (the influent) and from the adsorption column effluent.

The RSSCT set-up also allowed the provision for backwashing the adsorption columns. Effluent was directed straight to drain.

Apparatus Preparation.

Cleaning the RSSCT Rig

The PAC columns were removed from the test rig and then scrubbed and rinsed with deionised water to remove entrapped carbon. The sintered discs were also rinsed with deionised water to remove all traces of PAC.

Calcium carbonate residues sometimes adhered to the surface of the influent tanks. A brush was used to scrub the tank walls and the tanks rinsed with laboratory tap water.

All tanks, pipe-work and columns throughout the RSSCT Rig were rinsed with methylated spirit for a period of ½ hour. This was designed to remove any trace organic material that could have adhered to the surfaces of the RSSCT rig throughout previous tests. The rig was then rinsed thoroughly with tap water for a period of 1 hour before the next test commenced.

Preparation of the PAC.

GAC was placed into a pestle and motar and ground, effectively producing powdered activated carbon (PAC). The PAC was separated by hand using 150 and 180-micron sieves until the required amount of carbon was collected. This produced a 165-micron fraction for use in the RSSCT columns.

The PAC was rinsed with deionised water through a sieve until the rinse water ran clear. The PAC was then dried in the oven at approximately 100 °C for a period of 24 hours.

Figure 3.2 details the construction of the PAC columns.

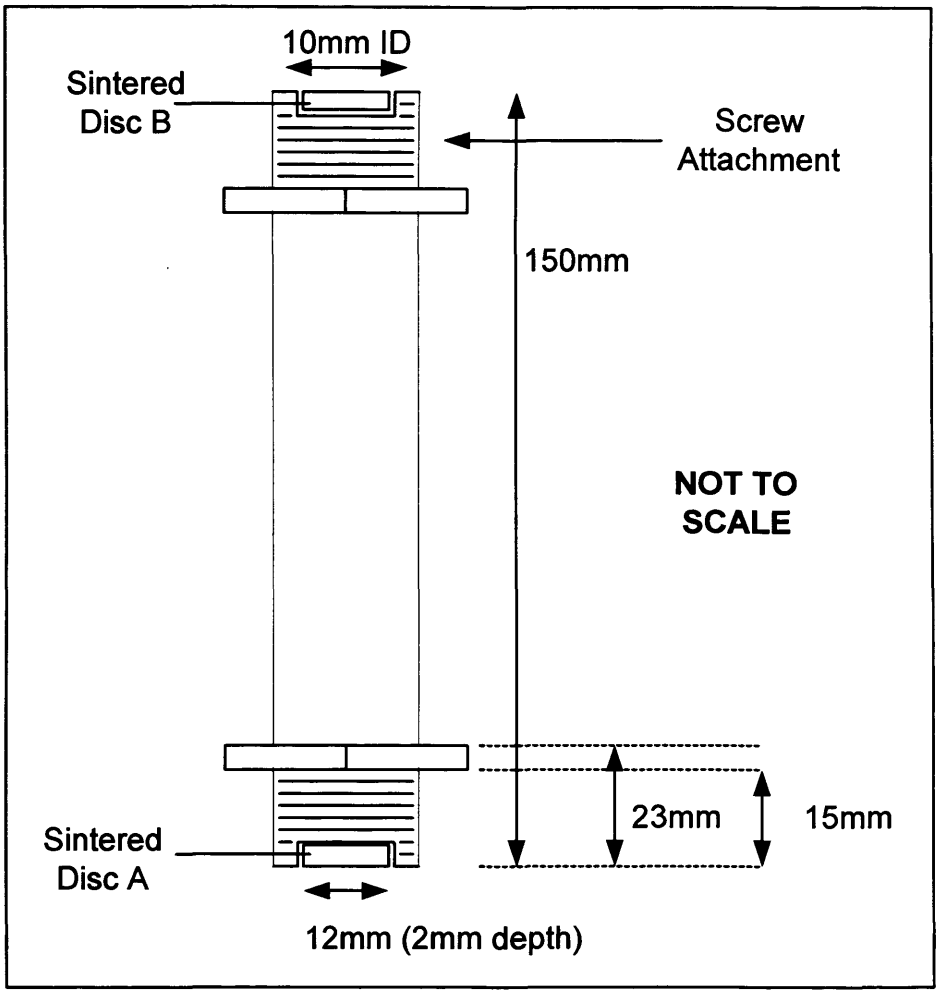


Figure 3.2. RSSCT PAC Column.

Sintered disc A was placed into the column and the bottom fitting screwed into place. A glass rod was inserted into the column and a pen was used to mark the top. An accurate balance was then used to measure out 0.75g of the prepared PAC. The PAC was then transferred into the column via a funnel and the column tapped to level the bed. The bed depth of the PAC was accurately measured using the previously marked glass rod. 0.75g PAC was found to produce a bed depth of approximately 18mm. A small amount of distilled water was placed into the column to wet the carbon. Care was taken not to overfill the column as this sometimes led to loss of the media. Sintered disc B was put into place and the whole of the column attached to the RSSCT rig ready for use.

Feed Water Preparation.

Ensuring the influent tanks were thoroughly clean, the tanks were filled to 160L with laboratory tap water. The appropriate quantity of fuel was added to the feed water using a syringe (refer to experimental work-plan, section 3.1.3).

Operating the RSSCT.

The rig was checked for leaks. If necessary PTFE tape was used to stop any leaks that may have occurred.

Only one carbon column was utilised in the experimental work-plan, hence the appropriate valves on the rig were closed before each test (refer to figure 3.1). The valve from influent tank number was then opened, followed by the valve to scaled flow meter (rotameter).

The peristaltic pump feeding the column was switched on ensuring the pressure did not exceed 2-bar. Initial pressure on the pump was high due to the water being forced through the carbon bed for the first time. The pump was altered during the run to compensate for any head loss. The flow meter was set to 5ml/ min. This gave an EBCT of 20s through the column.

To ensure the correct flow rate was maintained throughout the test, flow was verified daily using a 100ml measuring cylinder and stopwatch.

A flow rate of 5ml/ min was enough to provide the columns with influent for approximately 23 days.

Backwash Procedure.

The flow rate and pump pressure was monitored daily. If required, backwashing of the column was implemented throughout periods of increased head loss.

The pump and rotameter were switched off. The valve located on the influent sampling pipe was opened, followed by the valve from the backwash rotameter. A length of piping was attached to the backwash influent pipe and the other end to a laboratory water tap. The backwash rate was controlled from the tap. The column was tapped for a period of approximately 5 minutes with a wooden hammer to ensure that the compacted carbon was fluidised. This period was extended if required. Once finished, the valves were closed and the rig prepared for normal service.

Sampling Procedure.

All flow rates and pump pressures were monitored daily for the duration of the test. The temperature of the influent water was also monitored.

Samples from the RSSCT influent and effluent water were taken daily. The exact time of sampling was recorded in order to provide the required data for the EBCT and breakthrough curves. The samples were placed in clean 40ml vials and sealed with compatible vial caps (refer to section 3.3.1 for vial cleaning procedure). The 40ml vials used for sampling could be interfaced directly with the GC-MS autosampler. Influent water samples were taken directly from the influent tanks. Effluent samples were taken from the effluent sampling tap. Samples were taken as quickly as possible in order to avoid loss of the sample to the atmosphere. Aluminium foil was used to seal the vials whilst taking the effluent in order to reduce the amount of sample being lost to the atmosphere.

The samples were clearly labelled and individually sealed within plastic sampling bags. The samples were stored in a fridge (at 4°C) free of all other substances until time of analysis.

3.1.2. Revised RSSCT Design and Procedure.

A number of modifications were made to the RSSCT to resolve the practical problems detailed in section 3.4. These included;

- The addition of a cooler and circulating pump to the influent tanks. Note that a timer was used on the cooler to maintain the temperature at approximately 12°C.
- The addition of floating lids to the influent tanks.
- The replacement of the sintered discs within the PAC column.
- The addition of glass PAC columns to study the behaviour of the carbon bed in normal and backwash flow direction.
- Addition of glass PAC columns.

Figure 3.3 details the floating lids used on the modified RSSCT rig.

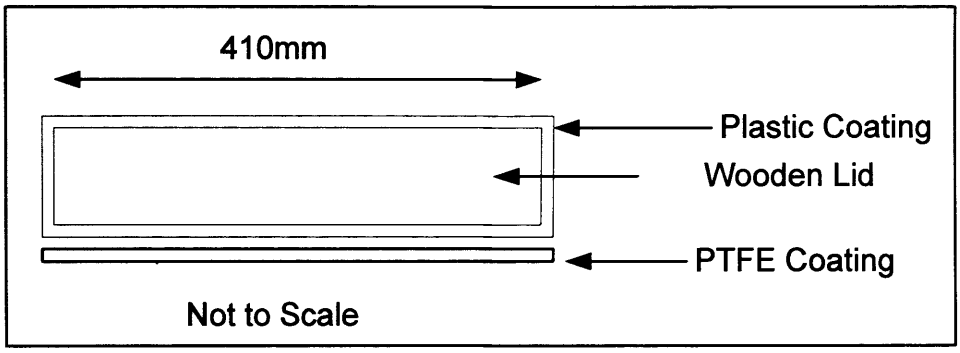


Figure 3.3. Floating Lid Construction.

Figure 3.4 illustrates the glass column construction.

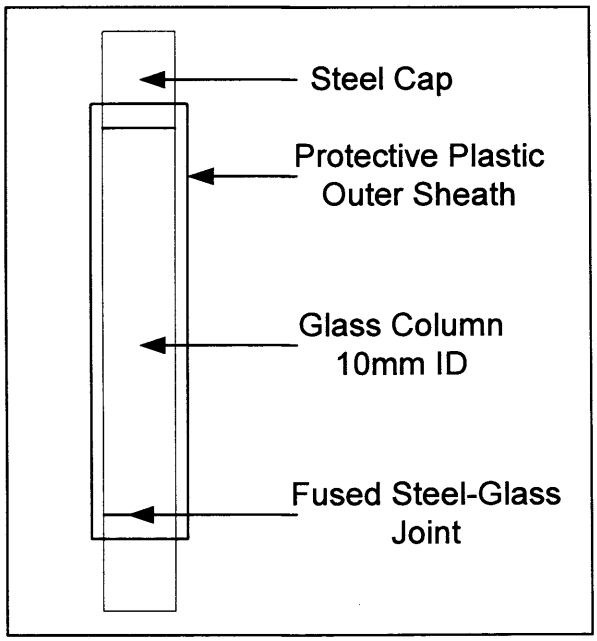


Figure 3.4. Glass PAC Column Construction.

Figure 3.5 details the modifications made to the RSSCT rig.

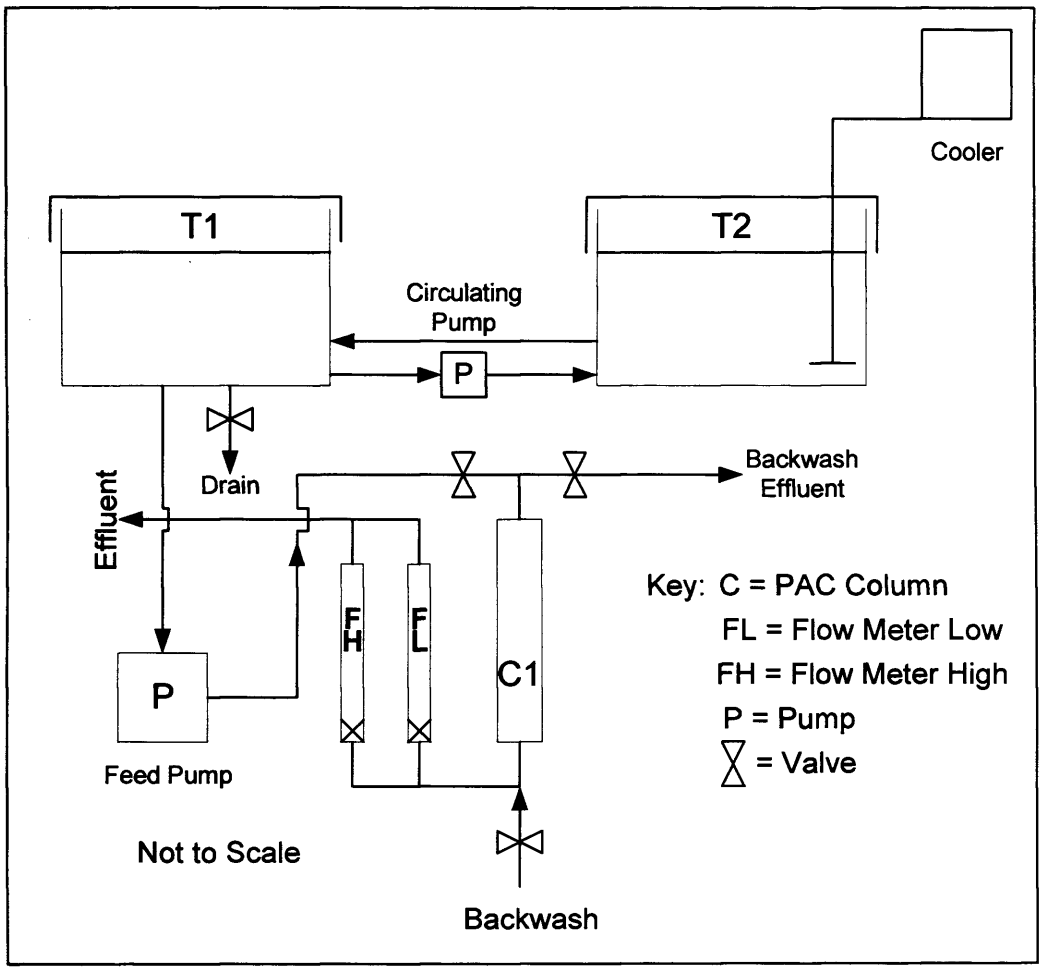


Figure 3.5. Modified RSSCT Rig.

The only change to the RSSCT procedure was that the cooler and circulating pump were switched on 12 hours before the start of each RSSCT run to allow the water to cool down to approximately 12°C.

3.1.3. RSSCT Work-Plan and Experimental Conditions.

Table 3.1 presents the RSSCT work-plan and experimental conditions.

	Pre-Test 1	Pre-Test 2	RSSCT Run 1	RSSCT Run 2	RSSCT Run 3
Period	30/08/00 - 06/09/00	08/09/00 - 12/09/00	18/05/01-13/06/01	26/06/01-20/07/01	22/08/01-13/09/01
Days Run	7	4	26	25	22
Fuel Type	Unleaded Gasoline	Unleaded Gasoline	Diesel	Diesel	Diesel
Target Concentration (µg/L)	-	-	40	2000	20,000
Wt. of fuel added (mg)	50	50	4.8	240	2400
Volume of water used (L)	160	160	120	120	120
Wt. Carbon Used (g)	0.75	0.75	0.75	0.75	0.75
Bed Depth (mm)	18	18	18	18	18
Flow Rate (ml/ min)	5	5	2.5	2.5	2.5
EBCT (s)	20	20	40	40	40

Table 3.1. RSSCT Work-Plan and Experimental Conditions.

3.2. Pilot-Plant Materials and Methodology.

One of the aims of the project was to test the simultaneous removal of MTBE and BTEX compounds using air-stripping and adsorption processes in series. Due to the limitations of the RSSCT and in order to introduce the required technologies, a laboratory-scale pilot-plant was designed and commissioned.

The aim of this section is to detail the design, operation and monitoring of the pilot-plant throughout the experimental period of the investigation. The section starts with the technical design of the pilot-plant. The design of the experimental work plan including the use of Taguchi orthogonal arrays will then be discussed. Finally, the operation of the pilot-plant will be detailed.

3.2.1. Air-Stripper and Adsorption Design.

Design equations for the adsorption columns and the air-stripper were considered and implemented wherever appropriate throughout the pilot-plant design period. The pilot-plant was designed by S. Hall and built within the Environmental Engineering Labs at UCL.

3.2.1.1. GAC Column Design.

Two types of carbon were tested throughout the experimental period; F400 and F600. Both carbons were produced by the Calgon Carbon Company. F400 has been extensively used within the water industry as a taste, odour and dissolved organic carbon (DOC) adsorbent and has been used for both surface and groundwater applications. F600 carbon has a highly developed pore structure and is marketed as an adsorbent for trace organic removal and MTBE removal. The manufacturers claim that the carbon is able to adsorb other organics at levels <1µg/L. F600 is specifically aimed at contaminated groundwater applications. Table 3.2 details some important properties of F400 and F600 GAC. Note that Iodine Number and Trace Capacity Number are defined in Section 1.6.2.3 of Chapter 1.

	F400	F600
Base Material	Bituminous Coal	Bituminous Coal
Effective Size (mm)	0.55-0.75	0.55-0.75
Bulk Density (g/cm^3)	0.44	0.63
Iodine No. (mg/g)	1000	850
Trace Capacity No. (mg/cm^3)	-	16

Table 3.2. Physical Properties of F400 and F400 Carbon.

One of the main considerations when designing the pilot-plant was that the carbon used in the columns would be GAC rather than PAC (which was used in the RSSCT).

Two 100mm diameter columns were used for GAC adsorption. Adverse hydraulic conditions caused by wall effects were considered when designing the adsorption columns. Lang *et al* (1993) suggested the ratio between filter column diameter and media diameter (D/d) should be >50, where D = diameter of carbon (mm) and d = diameter of column (mm).

For F400 and F600 carbon with an effective size of 0.55 - 0.75mm, the range of D/d was calculated to be 133 – 181. It can be seen that from the calculation of the D/d range, that the 100mm diameter columns would be large enough to prevent adverse hydraulic conditions caused by wall effects, hence minimising short-circuiting down the column walls.

Required Flow Rate.

From literature (Pontius, 1990), the hydraulic application rate for GAC columns used in water treatment applications was cited as 7-10m/h. For the purpose of the pilot-plant a hydraulic application rate of 8m/h was used. The hydraulic application rate, the volumetric flow rate and surface area of a column are related by the following equation;

$$V = \frac{Q}{A} \qquad \textbf{(eqn 3.1)}$$

Where V = hydraulic application rate (m/h), Q = Flow rate (m^3/hr) and A = surface area (m^2).

Assuming an effective area of $7.85 \times 10^{-3} m^2$ (diameter of 0.1m) the required flow rate to maintain a hydraulic application rate of 8m/h was calculated as 1.05L/min. Hence 1.05L/min represented the flow rate required from the air-stripper effluent to supply the GAC columns. Note that the total flow rate through the air-stripping column was required to be a minimum of 2.1L/min (assuming 2 adsorption columns).

EBCT.

The EBCT was calculated for each successive bed depth through the GAC columns where;

$$EBCT = \frac{\text{bed volume}}{\text{flow rate}} \qquad \textbf{(eqn 3.2)}$$

Three bed depths were regularly sampled during the experimental phase; 25mm, 50mm and 175mm. Table 3.3 details the bed volume and EBCTs for each of the three bed depths.

Bed Depth (mm)	Bed Volume (m^3)	EBCT (seconds)
25	1.96×10^{-4} m^3	11.2
50	3.93×10^{-4} m^3	22.4
175	$1.37 \times 10^{-3} m^3$	78.3

Table 3.3. Calculated Bed Volumes and EBCT.

3.2.1.2. Air-Stripper Design.

Packing Type.

High performance stainless steel structured packing (type HS10) was investigated and found to be a suitable packing material for use within the air-stripper. The HS10 structured packing provided by Koch-Glitsh has higher theoretical removal efficiency than random packing, due to its greater surface area.

High performance stainless steel packing such as the type used within the pilot-plant have not yet been used within the water industry. However, after investigation the steel used for the packing was found to be suitable for use within the industry.

Three steels are listed by the DWI as being suitable for use within the water industry; 1.4307, 1.4404 and 1.4462. The HS10 structured packing can be manufactured to either standard 1.4307 or 1.4404.
A full list of steels can be found on the DWI web site

Air-Stripper Design Equations.

As discussed in Section 1.6.1.3 of Chapter 1, previous authors cite four equations for the design of air-stripper units, based on mass transfer theory. Relevant equations were found in; Ball *et al*, 1984, Perry and Green, 1984 and Dzombak *et al*, 1993. Referring to Section 1.6.1.3 of Chapter 1 the height of packed tower (m) was calculated using equations 1.6 – 1.9, assuming an effluent water flow rate of 2.1L/min (two adsorption columns running at 1.05L/min).
As the calculation of packing height requires known air and water flow rates and influent and effluent concentrations, the following scenarios were devised for the design of the pilot plant (Table 3.4).

	Air-to-Water Ratio	Influent Conc. (μg/L)	Required Effluent Conc. (μg/L)
MTBE	100	40	5
MTBE	100	5	0
MTBE	10	40	5
MTBE	10	5	0
Benzene	100	100	1
Benzene	100	40	1
Benzene	10	100	1
Benzene	10	40	1

Table 3.4. Devised Scenarios for Air-Stripping Design.

Note that the air-to-water ratios presented above were different from the actual ratios implemented throughout the experimental phase. This was due to the low water flow rates experienced within the laboratory, in-turn caused by the low head pressure of the water within the laboratory.

Referring to equation 1.7 (Section 1.6.1.3 of Chapter 1), the calculation of HTU requires the mass transfer coefficient for the particular application. Since the application of the packing material was within the fuel oil study was novel, the mass transfer coefficient had not been previously calculated or cited in relevant literature.

For a novel application the mass transfer coefficient can be determined in pilot-scale tests (Ball *et al*, 1984 and Kavanaugh and Trussell, 1980), yet the mass transfer coefficient is needed to calculate the height of packing of the air-stripping column required to run the experiments.

The Onda correlation was used to derive the mass transfer coefficient for the application.

Note that values for L and G (the liquid and gas loading rate) were calculated using the known air and water flow rates and the number of moles of each medium. The number of moles was calculated by;

$$n = \frac{m}{M} \qquad \textbf{(eqn 3.3)}$$

Where n = number of moles of the substance, m = mass of substance (g) and M = molecular weight of substance (g mol^{-1}).

Values were obtained for the calculation of the mass transfer coefficient and are presented in Table 3.5 (expressed at 20°C). Note that L and G values were changed accord to the scenarios presented in table 3.4.

		Value	Unit			Value	Unit
τ_p		0.075	N/m	**L**	air:water 100	1.9	mol/s
τ_L		0.073	N/m		air:water 10	1.9	mol/s
μ_L		0.00089	Nsm^{-2}	**G**	air:water 100	0.15	mol/s
μ_G		0.000017	Nsm^{-2}		air:water 10	0.015	mol/s
P_L		998	Kg/m^3	**G**		9.8	m/s^2
P_G		1.205	Kg/m^3	a_t		500	m^2/m^3
D_L	MTBE	m^2/s	8.2×10^{-10}	**H**	MTBE	0.018	-
	Benzene	m^2/s	8.9×10^{-10}		Benzene	0.22	-
D_G	MTBE	m^2/s	9.8×10^{-6}				
	Benzene	m^2/s	9.5×10^{-6}				
D_p		0.15	M				

Table 3.5. Onda Correlation Values. Source; Coulson and Richardson, 1983, Perry and Green, 1984.

An Excel spreadsheet was developed in which the mass transfer coefficient was calculated using equations 1.10 – 1.13, referring to data presented in Table 3.5. The Excel spreadsheet allowed variables to be changed depending upon the contaminant type and liquid and gas loading rates. Tables 3.6 – 3.7 present the derived Onda correlation for the conditions detailed in Table 3.4.

Benzene - High air:water		Unit
τ_p	0.075	N/m
τ_L	0.073	N/m
L	1.9	mol/s
G	0.15	mol/s
a_t	500	m^2/m^3
μ_L	$8.9x10^{-4}$	Nsm^{-2}
μ_G	$1.7x10^{-5}$	Nsm^{-2}
G	9.8	m/s/s
d_p	0.13	m
P_L	998	Kg/m^3
P_G	1.205	Kg/m^3
D_L	$8.9x10^{-10}$	m^2/s
D_G	$9.5x10^{-6}$	m^2/s
a	b	c
1.02	1.16	1.54
d	e	f
0.16	0.02	5.40
g	h	i
0.03	5.31	0.005
j	k	l
7.46	1.14	0.0002
a_w/a_t	0.34	
a_w	170.2	m^2/m^3
k_L	$9.5x10^{-5}$	
k_g	$5.0x10^{-5}$	
H	0.22	
$(k_La)^{-1}$	714.3	
k_La	0.001	s^{-1}
	5.04	$\mathbf{h^{-1}}$

Benzene – Low air:water		Unit
τ_p	0.075	N/m
τ_L	0.073	N/m
L	1.9	mol/s
G	0.015	mol/s
a_t	500	m^2/m^3
μ_L	$8.9x10^{-4}$	Nsm^{-2}
μ_G	$1.7x10^{-5}$	Nsm^{-2}
G	9.8	m/s/s
d_p	0.13	m
P_L	998	kg/m^3
P_G	1.205	kg/m^3
D_L	$8.9x10^{-10}$	m^2/s
D_G	$9.5x10^{-6}$	m^2/s
a	b	c
1.02	1.16	1.54
d	e	f
0.16	0.02	5.40
g	h	i
0.03	5.31	0.005
j	k	l
1.49	1.14	0.0002
a_w/a_t	0.34	
a_w	170.2	m^2/m^3
k_L	$9.5x10^{-5}$	
k_g	$9.9x10^{-6}$	
H	0.22	
$(k_La)^{-1}$	3332.1	
k_La	0.0003	s^{-1}
	1.08	$\mathbf{h^{-1}}$

Table 3.6. Mass Transfer Calculations for Benzene.

MTBE - High air:water		Unit
τ_p	0.075	N/m
τ_L	0.073	N/m
L	1.9	mol/s
G	0.15	mol/s
a_t	500	m^2/m^3
μ_L	$8.9x10^{-4}$	Nsm^{-2}
μ_G	$1.7x10^{-5}$	Nsm^{-2}
g	9.8	m/s/s
d_p	0.13	m
P_L	998	Kg/m^3
P_G	1.205	Kg/m^3
D_L	$8.2x10^{-10}$	m^2/s
D_G	$9.8x10^{-6}$	m^2/s
a	b	c
1.02	1.16	1.54
d	e	f
0.16	0.02	5.40
g	h	i
0.03	5.31	0.005
j	k	l
7.46	1.13	0.0002
a_w/a_t	0.34	
a_w	170.16	m^2/m^3
k_L	$9.1x10^{-5}$	
k_g	$5.1x10^{-5}$	
H	0.018	
$(k_La)^{-1}$	6831.7	
k_La	0.0001	s^{-1}
	0.53	$\mathbf{h^{-1}}$

MTBE - Low air:water		Unit
τ_p	0.075	N/m
τ_L	0.073	N/m
L	1.9	mol/s
G	0.015	mol/s
a_t	500	m^2/m^3
μ_L	$8.9x10^{-4}$	Nsm^{-2}
μ_G	$1.7x10^{-5}$	Nsm^{-2}
G	9.8	m/s/s
d_p	0.13	m
P_L	998	kg/m^3
P_G	1.205	kg/m^3
D_L	$8.2x10^{-10}$	m^2/s
D_G	$9.8x10^{-6}$	m^2/s
a	b	c
1.02	1.16	1.54
d	e	f
0.16	0.02	5.40
g	h	i
0.03	5.31	0.005
j	k	l
1.49	1.13	0.0002
a_w/a_t	0.34	
a_w	170.16	m^2/m^3
k_L	$9.1x10^{-5}$	
k_g	$1.0x10^{-5}$	
H	0.018	
$(k_La)^{-1}$	33981.5	
k_La	0.00003	s^{-1}
	0.11	$\mathbf{h^{-1}}$

Table 3.7. Mass Transfer Calculation for MTBE.

Referring to equation 1.7 (Section 1.6.1.3 of Chapter 1), the mass transfer coefficient can also be determined experimentally using data obtained from the pilot-plant. As part of the results chapter of the study, comparisons of the Onda derived value and the experimentally derived mass transfer values are made.

Calculation of Required Packed Column Height.

Based upon the Onda derived mass transfer coefficient, the height of the packing was calculated using equations 1.6. - 1.9. These are presented in Tables 3.8 - 3.9.

Benzene - High air:water		
	Value	**Unit**
L	9.7	m^3/m^2h
G	970	m^3/m^2h
C_{in}	100	µg /L
C_{out}	1	µg /L
K_La	5.04	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
Air:water	100	-
P	1	atm
H	0.22	-
P_d	0.018	m^2
R	18	-
NTU	4.8	-
HTU (m)	1.9	m
Z	9.3	m

Benzene – Low air:water		
	Value	**Unit**
L	9.7	m^3/m^2h
G	97	m^3/m^2h
C_{in}	100	µg /L
C_{out}	1	µg /L
K_La	1.08	h^{-1}
Q_w	2.1	L/min
Q_a	210	L/min
air:water	10	-
P	1	atm
H	0.22	-
P_d	0.018	m^2
R	1.8	-
NTU	8.6	-
HTU (m)	9.0	m
Z	76.9	m

Benzene - High air:water		
	Value	**Unit**
L	9.7	m^3/m^2h
G	970	m^3/m^2h
C_{in}	40	µg /L
C_{out}	1	µg /L
K_La	5.04	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
Air:water	100	-
P	1	atm
H	0.22	-
P_d	0.018	m^2
R	18	-
NTU	3.8	-
HTU (m)	1.9	m
Z	7.4	m

Benzene – Low air:water		
	Value	**Unit**
L	9.7	m^3/m^2h
G	97	m^3/m^2h
C_{in}	40	µg /L
C_{out}	1	µg /L
K_La	1.08	h^{-1}
Q_w	2.1	L/min
Q_a	210	L/min
air:water	10	-
P	1	atm
H	0.22	-
P_d	0.018	m^2
R	1.8	-
NTU	6.5	-
HTU (m)	9.0	m
Z	58.8	m

Table 3.8. Height of Packing based upon Benzene.

MTBE - High air:water		
	Value	Unit
L	9.7	m^3/m^2h
G	970	m^3/m^2h
C_{in}	40	µg /L
C_{out}	5	µg /L
K_La	0.53	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
air:water	100	-
P	1	atm
H	0.018	-
P_d	0.018	m^2
R	1.7	-
NTU	3.3	-
HTU (m)	18.3	m
Z	335.0	m

MTBE – Low air:water		
	Value	Unit
L	9.7	m^3/m^2h
G	97	m^3/m^2h
C_{in}	40	µg /L
C_{out}	5	µg /L
K_La	0.11	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
air:water	100	-
P	1	atm
H	0.018	-
P_d	0.018	m^2
R	0.17	-
NTU	-	-
HTU (m)	88.2	m
Z	-	m

MTBE - High air:water		
	Value	Unit
L	9.7	m^3/m^2h
G	970	m^3/m^2h
C_{in}	5	µg /L
C_{out}	1	µg /L
K_La	0.53	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
air:water	100	-
P	1	atm
H	0.018	-
P_d	0.018	m^2
R	1.7	-
NTU	2.4	-
HTU (m)	18.3	m
Z	43.3	m

MTBE – Low air:water		
	Value	Unit
L	9.7	m^3/m^2h
G	97	m^3/m^2h
C_{in}	5	µg /L
C_{out}	1	µg /L
K_La	0.11	h^{-1}
Q_w	2.1	L/min
Q_a	21	L/min
air:water	10	-
P	1	atm
H	0.018	-
P_d	0.018	m^2
R	0.17	-
NTU	-	-
HTU (m)	88.2	m
Z	-	m

Table 3.9. Height of Packing based upon MTBE.

It can be noted from tables 3.8 – 3.9 that if the Onda derived mass transfer coefficients were implemented in the design of the pilot plant, the required packing height of the air-stripping column would be too great for the remit of the fuel oil study. Note also that when low air-to-water ratios were implemented, the model suggests that MTBE would not be removed at all. This can be attributed to

the stripping factor. If the stripping factor is <1, removal by air-stripping is theoretically not possible.

Referring to literature, mass transfer coefficients for VOCs with similar Henry's Law Constants and using full-scale air-stripping columns, are typically 1 order of magnitude greater than those calculated as part of the fuel oil study (Ball *et al*, 1984). If these mass transfer coefficients were substituted into equations 1.6 - 1.9, then the required height of packing for the pilot-scale column would then be applicable to the small-scale air-stripping column. Under the conditions detailed in Table 3.4, the mass transfer coefficient can be increased if parameters such as the air-to-water ratio are increased. If these values were then substituted into equations 1.6 – 1.9, the required height of the packing would also be suitable for use within the pilot-scale air-stripping column.

The height of the packing and the diameter of the packing were ultimately based upon similar pilot-plant column designs found in literature (Ball *et al*, 1984, Perry and Green, 1984 and Dzombak *et al*, 1993). This in turn was based upon the required influent water flow rate of the adsorption columns calculated in equation 3.1. The design of the air-stripper packing material was verified by the manufacturer (Koch-Glitsh).

3.2.2. Pilot-Plant Technical Design.

The following section details the technical drawings of the pilot-plant. All components for the pilot-plant were designed and built by S. Hall within the Environmental Engineering Labs, UCL.

Figure 3.6 details the process flow diagram of the pilot-plant.

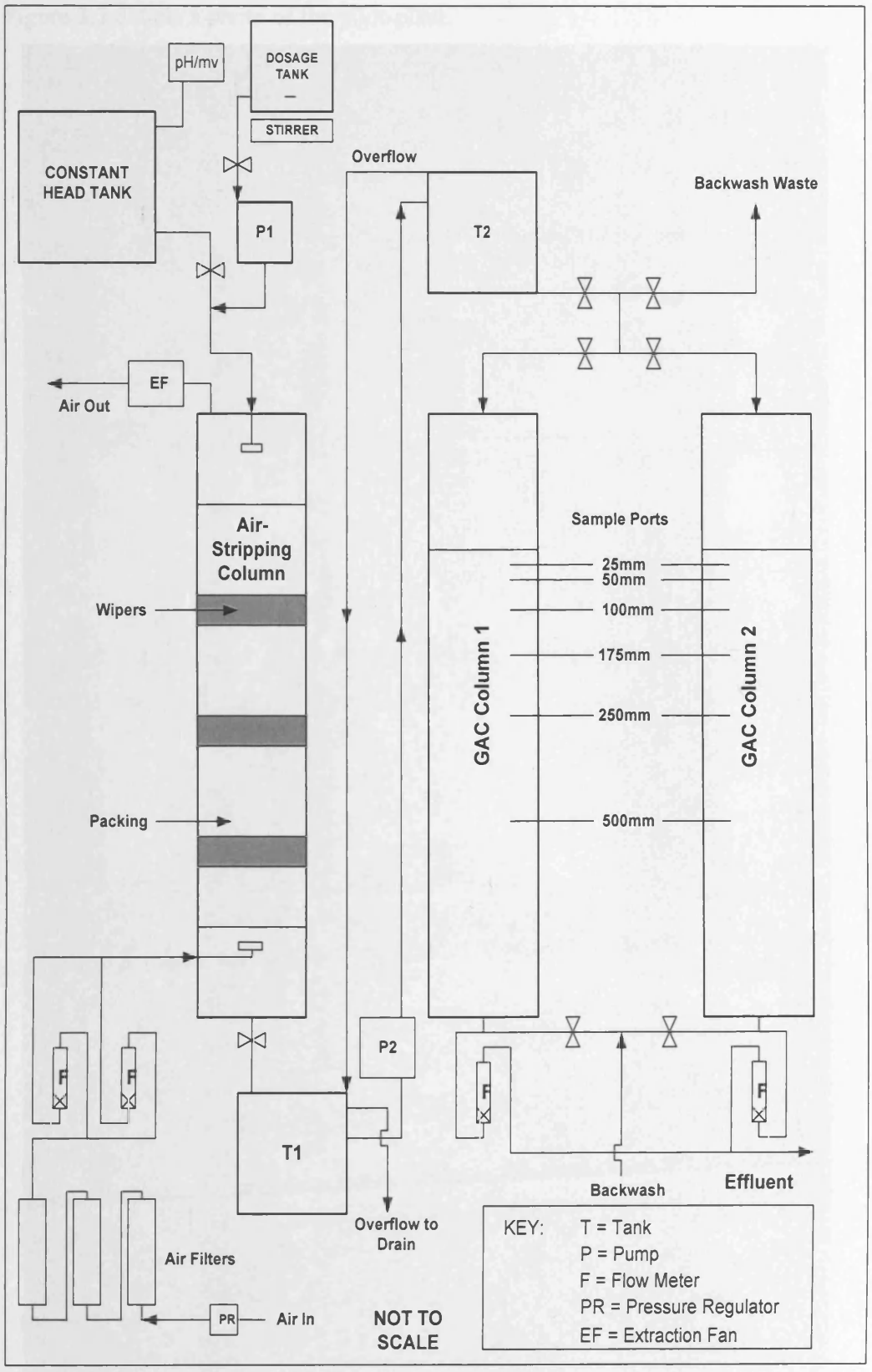


Figure 3.6. Process Flow Diagram of Pilot-Plant.

Figure 3.7 details a photo of the pilot-plant.

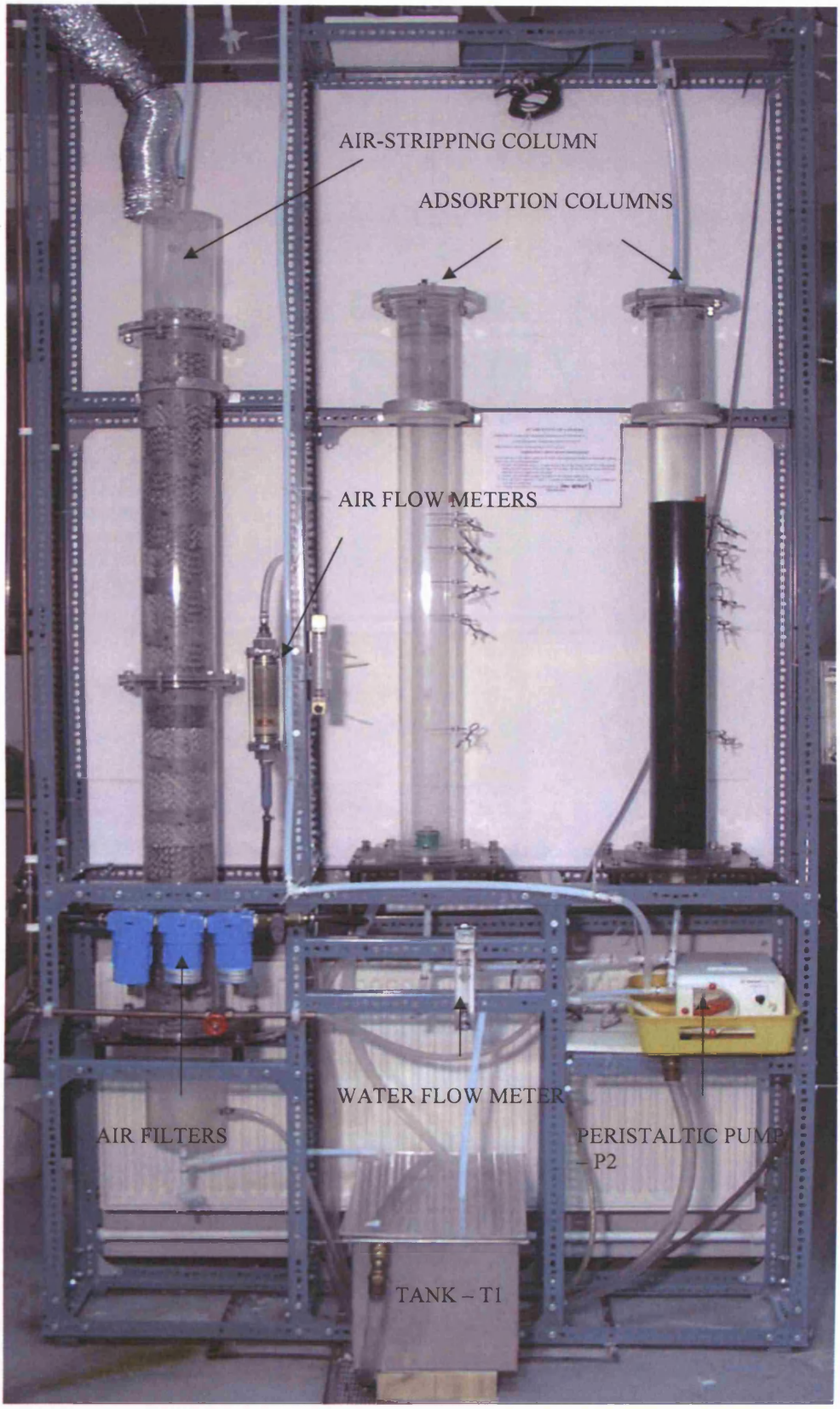


Figure 3.7. Photo Detail of Pilot-Plant.

Figure 3.8 details the technical design of the air-stripping column.

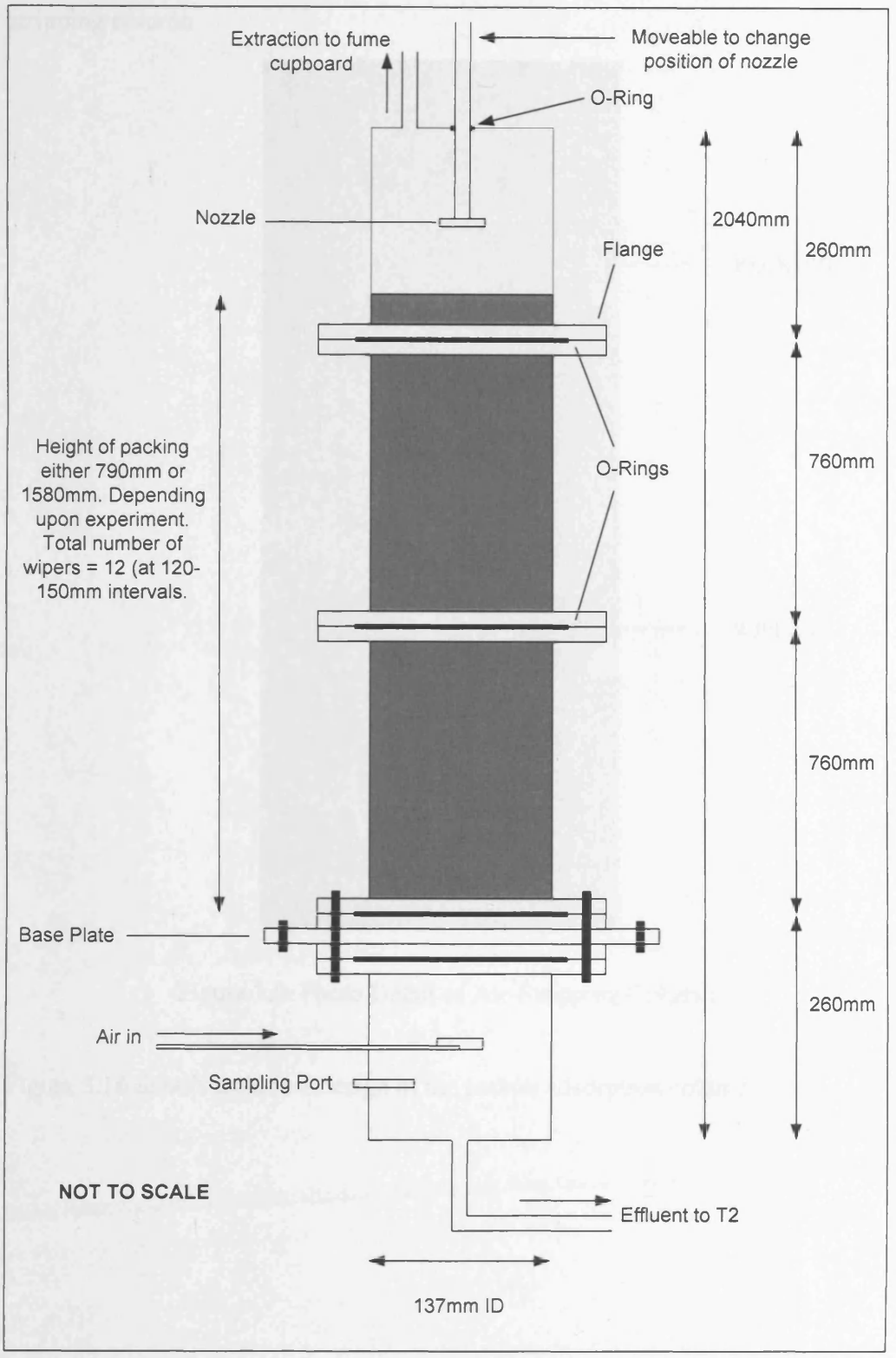


Figure 3.8. Design Detail of Air-Stripping Column.

Figure 3.9 details a section of the packing material mounted within the air-stripping column.

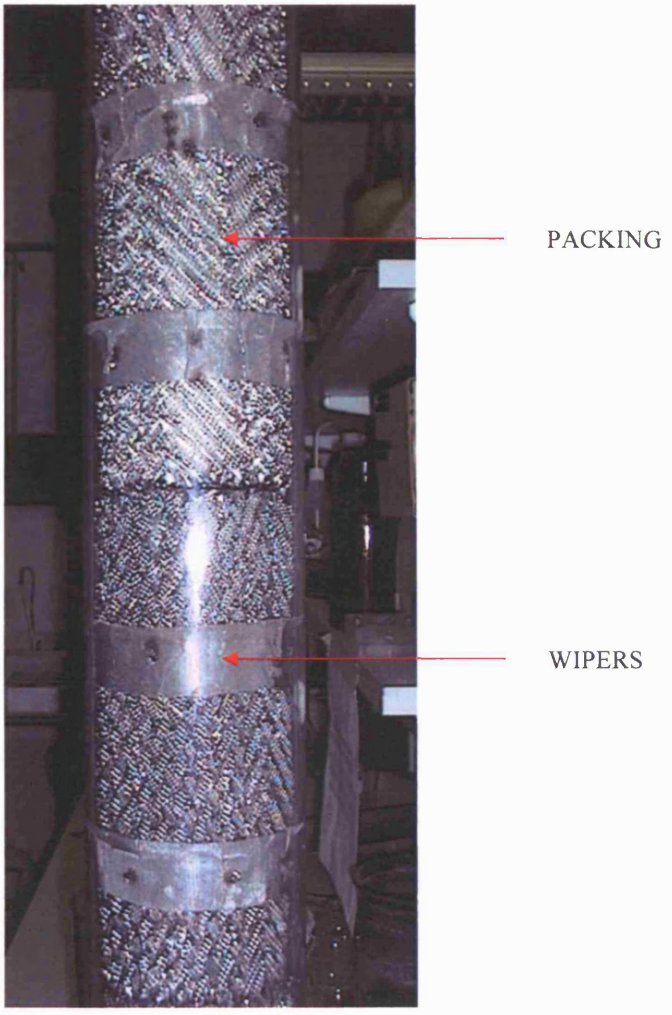


Figure 3.9. Photo Detail of Air-Stripping Column.

Figure 3.10 details technical design of the carbon adsorption columns.

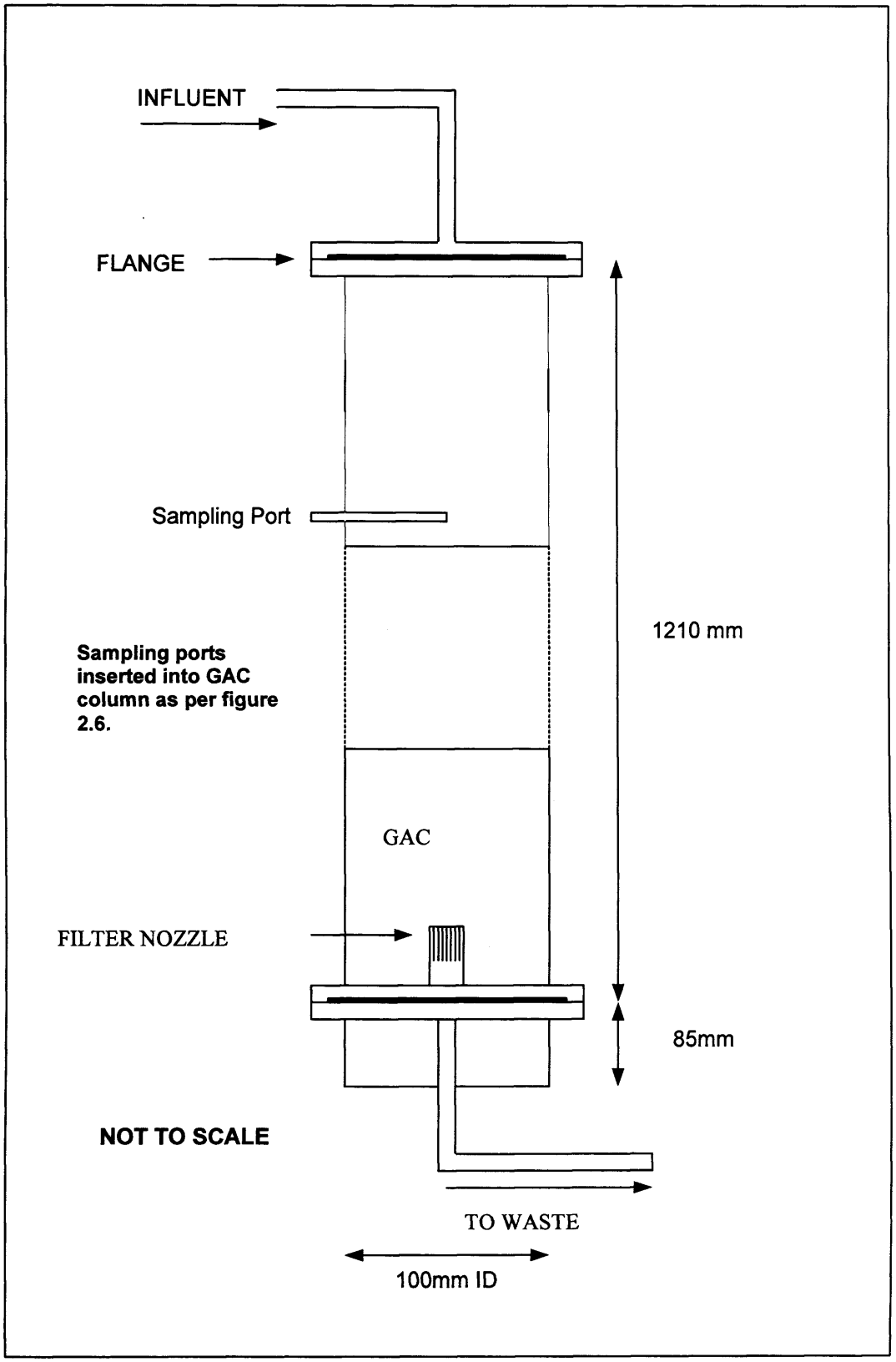


Figure 3.10 Design Detail of Carbon Adsorption Column.

The design of the pilot-plant ensured that a number of process parameters could be adjusted as part of the experimental plan. These include; air flow rates, water flow rates, air-stripping packing depth, bed depth of GAC, EBCTs and influent concentrations of BTEX/ MTBE compounds.

Construction Materials.

Wherever possible the pilot-plant was constructed with non – BTEX and MTBE adsorbing material. Head tanks, where the water had an approximate retention time of 16-21 min were made of stainless steel. All tubing and valves throughout the rig were made of PTFE and were replaced between tests. Peristaltic tubing was made of Fluorel, a non - BTEX/ MTBE adsorbing material. Again, this was replaced between tests.

Perspex is known not to be compatible with BTEX/ MTBE compounds, with some adsorption onto the plastic expected. However, preliminary tests showed that adsorption of BTEX/ MTBE compounds onto the Perspex columns was not significant. This was believed to be due to the low retention time of the water flowing through the columns and the low influent concentrations used. The possible desorption of organic material from the Perspex columns was investigated by running the air-stripper and GAC columns with clean water after tests had finished. GC-MS analysis was then carried out on the effluent water and showed that MTBE and BTEX compounds were not present in solution.

3.2.3. Pilot-Plant Method of Operation.

The entire pilot-plant detailed in section 3.2.2 was mounted within a stainless steel (Dexion) frame measuring $3 \times 1.5 \times 0.3$m. Effluent from the pilot-plant was directed straight to drain.

Mains water feeding the pilot-plant supplied a constant head tank. Level in the constant head tank was regulated by a ball valve and was measured volumetrically. A pH, mv and temperature logger was fitted to the constant head tank to monitor influent water quality. Total dissolved solids (TDS) and total hardness were also monitored.

BTEX/ MTBE concentrate was dosed in-line to the water leaving the constant head tank. Mixing of the water-concentrate was ensured using a specially

designed injection port and static mixer. Figure 3.11 illustrates the injection port and static mixer.

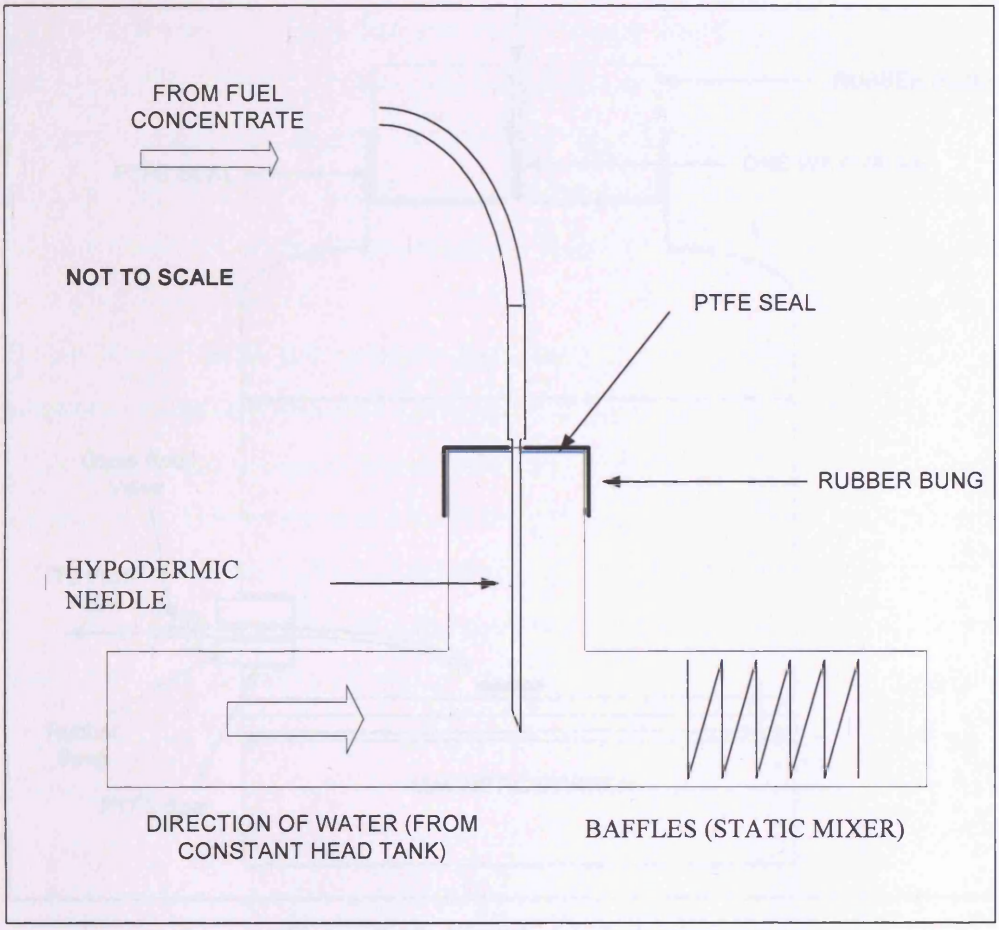


Figure 3.11. Concentrate Injection Port.

Methyl blue was used as a dye tracer to test the efficiency of the injection port. Methyl blue, which had been injected into the influent water (flowing from the constant head tank) exited the static mixer as one continuous (diluted) colour. If mixing had not occurred, pulses of colour would have been observed.

BTEX/ MTBE concentrate used throughout each test was stored in a modified 10L aspirator. See figure 3.12 for the modified aspirator design.

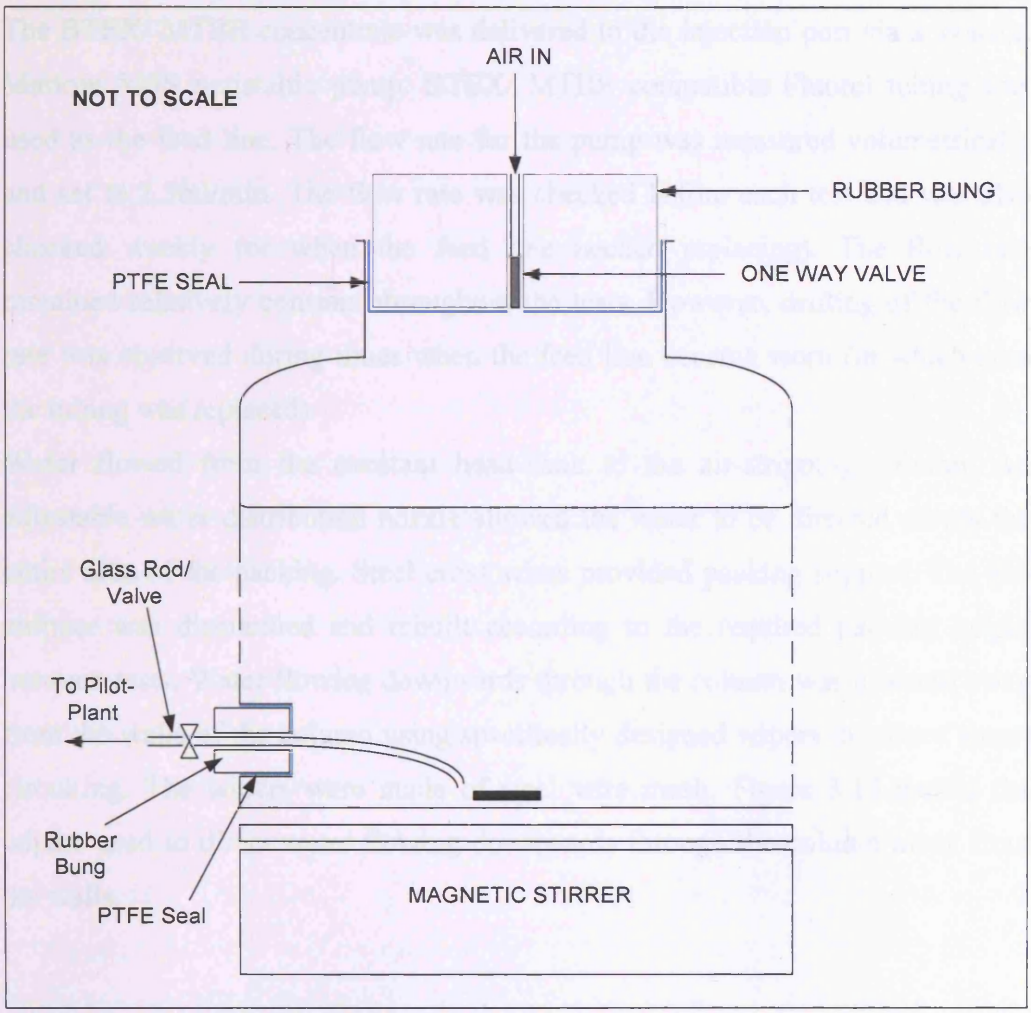


Figure 3.12. Modified 10L Aspirator.

For the aspirator lid, a hole was drilled through a rubber bung and a one-way valve was inserted. The one-way valve was designed to allow the level of the BTEX/ MTBE solution to fall, whilst ensuring vapours did not escape the aspirator. The bung was lined with PTFE tape to avoid contact between the rubber and the solution. The lower exit from the aspirator was also fitted with a modified rubber bung. A hole was drilled through the rubber and a glass rod and valve fitting inserted. A length of Fluorel tubing was attached to the end of the glass rod protruding into the aspirator, in order to maximise the amount of solution that could be extracted from the vessel without having to refill. The rubber bung was coated in PTFE tape to avoid contact between the rubber and the solution. Both bungs were dismantled, washed thoroughly with deionised water and re-assembled before each test commenced.

The BTEX/ MTBE concentrate was delivered to the injection port via a Watson Marlow 505S peristaltic pump. BTEX/ MTBE compatible Fluorel tubing was used as the feed line. The flow rate for the pump was measured volumetrically and set at 2.5ml/min. The flow rate was checked before each test and was also checked weekly (or when the feed line needed replacing). The flow rate remained relatively constant throughout the tests. However, drifting of the flow rate was observed during times when the feed line became worn (in which case the tubing was replaced).

Water flowed from the constant head tank to the air-stripping column. An adjustable water distribution nozzle allowed the water to be directed across the entire area of the packing. Steel cross wires provided packing support. The air-stripper was dismantled and rebuilt according to the required packing height between tests. Water flowing downwards through the column was directed away from the walls of the column using specifically designed wipers to reduce short-circuiting. The wipers were made of steel wire mesh. Figure 3.13 details the wipers used to direct water flowing downwards through the column away from the walls.

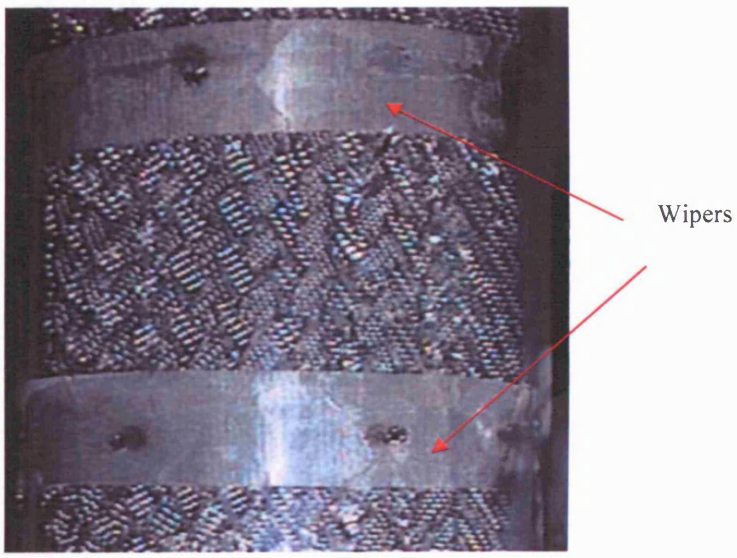


Figure 3.13. Photo Detail of Wipers within Air-Stripping Column.

A test was carried out to examine whether the wipers successfully prevented the water from flowing down the side of the column. Methyl blue was injected into the influent water. Observations were then made as to whether the coloured water exited the air-stripping column uniformly, or in pulses. Throughout the test although the continuous nature of the coloured water exiting the air-stripping column suggested limited short-circuiting, water was observed running down the side of the column. The wipers appeared to aid the redirection of the water away from the walls, however, the water did not remain within the centre of the packing for the entire length of the column.

A Mattei 200 Series Rotary Vane Air Compressor supplied the air to the pilot-plant. The compressor was able to sustain the required air flow rates needed for each experiment, 24 hours/day, for the duration of the tests. An adjustable pressure valve was fitted in line to regulate the air from the compressor as it entered the pilot-plant. Due to the fact that the compressor took air from a busy street with heavy volumes of traffic, the air was passed through a series of filters before it entered the air-stripping column to remove potential petrochemical contaminants. This was in addition to the filters incorporated within the air compressor system. An elevated hydrocarbon concentration within the air-stripper could affect the concentration gradient needed for mass transfer within the air-stripper column. Three air-filters were supplied by Alpha Controls Ltd; G10P + G10H + G10C. These filters were recommended for the removal of hydrocarbons from air intended for air-stripping. The filters were able to operate within the flow rates and pressures used in the experiments and were all fitted with automatic drain valves to remove moisture.

Two Platon air rotameters regulated the flow rate of the air entering the air-stripper; one for low flow rates and one for high flow rates.

Water leaving the air-stripping column was collected in a 45L steel tank. The tank was covered with an unsealed PTFE lid. A Gelman Sciences Posi-flow II peristaltic pump moved water to a second 45L steel head tank located above the adsorption column. The lids to the head tanks were not sealed in order to maintain atmospheric pressure. A build-up of negative pressure within the tanks may have caused the pump to fail. Flow rates provided by the pump spanned the entire range required by the experimental phase. Water from the head tank provided the influent water for the adsorption columns. Platon flow meters

(rotameters) located at the bottom of the adsorption columns regulated the water flow rates through each column. An overflow from the head tank directed water into the lower tank, which was fitted with an overflow directly to drain. Carbon depth was measured to a predetermined mark on the adsorption column, corresponding to several sampling ports. Sampling ports were fitted to the column at 25mm, 50mm, 175mm and 200mm. Figure 3.14 illustrates the design of the sampling ports.

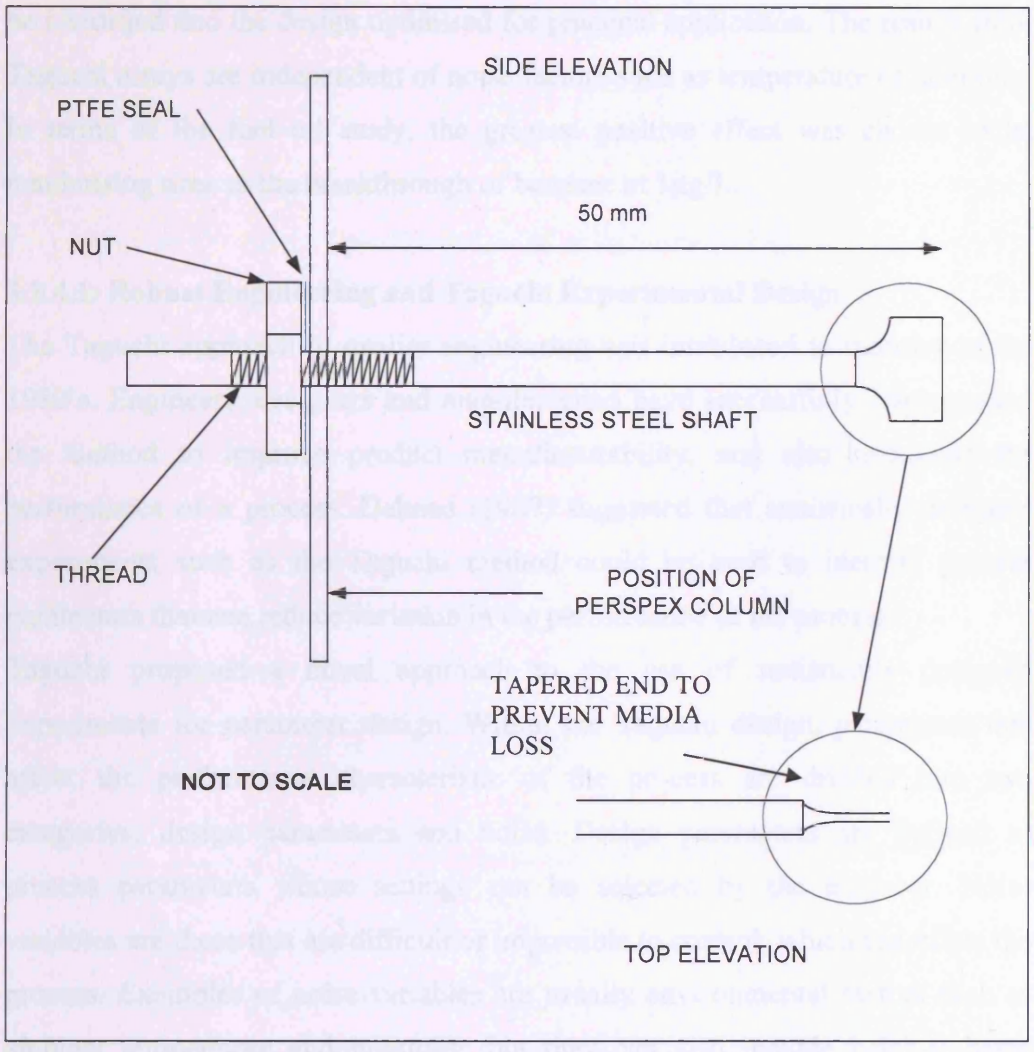


Figure 3.14. Adsorption Column Sampling Ports.

Backwash water for the GAC columns was supplied by a separate lab tap water source, plumbed in to the bottom of the rig. Opening and closing the appropriate valves implemented backwashing of the adsorption columns.

3.2.4. Taguchi Experimental Design.

The number of parameters that could be assessed between pilot-plant experiments was large. For this reason Taguchi orthogonal arrays were used to statistically construct the experimental work plan. Orthogonal arrays allow the maximum amount of information to be gained from the minimum number of tests. Analysis of the arrays once all the experiments have been completed enables the parameter(s) that has the greatest positive effect upon the process to be identified and the design optimised for practical application. The results from Taguchi arrays are independent of noise factors such as temperature or humidity. In terms of the fuel oil study, the greatest positive effect was chosen to be maximising time to the breakthrough of benzene at 1μg/L.

3.2.4.1. Robust Engineering and Taguchi Experimental Design.

The Taguchi approach to quality engineering was introduced to industry in the 1980's. Engineers, designers and manufacturers have successfully implemented the method to improve product manufacturability, and also maximise the performance of a process. Dehnad (1989) suggested that statistically designed experiments such as the Taguchi method could be used to identify process parameters that can reduce variation in the performance of the process.

Taguchi proposed a novel approach to the use of statistically designed experiments for parameter design. Within the Taguchi design, parameters that affect the performance characteristic of the process are divided into two categories; design parameters and noise. Design parameters are defined as process parameters whose settings can be selected by the engineer. Noise variables are those that are difficult or impossible to control, which can effect the process. Examples of noise variables are usually environmental factors such as ambient temperature and humidity, but they can also include batch-to-batch variation of raw materials and the use of different operators.

Through a series of statistically designed experiments, the Taguchi method aims to maximise the robustness of a design for a particular application, where a process that does not change with the influence of noise is described as being robust. Ensuring the robust design of a process can ensure that the quality of the end process is high. Roy (2001) described robust engineering as an optimisation strategy that can be used in the development of new technologies, in terms of

both process and product design. Robust engineering can represent the application of the Taguchi Method at the R&D level and at process optimisation level. It is at the process optimisation level that the air-stripping and adsorption technologies employed in the fuel oil study are concerned. Roy (2001) stated that the Taguchi method of experimental design concentrated on identifying the ideal function (or functions) of a particular product or process design. The best values for design parameters that optimise the performance of the process can then be selected, even with the presence of external noise factors such as temperature or humidity.

3.2.4.2. Orthogonal Arrays.

The traditional method of studying a large number of process variables usually involves the review of each variable, one at a time. With such a large number of parameters available to implement between tests and the fact that each test may have taken up to four weeks to complete, studying each variable independently would have represented an inefficient and costly approach to the experimental phase of the study.

Orthogonal arrays form the basis of the Taguchi experimental design. Dehnad (1989) stated that grouping variables into such suitable orthogonal arrays means that the researcher can extract much more precise information than if experiments were conducted with a single-factor by single-factor approach. A planned series of matrix experiments using orthogonal arrays represents an efficient way of studying the effect of several factors simultaneously. A suitably designed orthogonal array (or matrix) is used to determine how the values of the parameters are altered between tests, so that the effect of each parameter can then be separated at the end of the study.

The implementation of orthogonal arrays can have many benefits. First, the conclusions drawn from such experiments are valid over the entire experimental region spanned by the control parameters and their settings. Secondly, there is a large saving in the experimental effort. Finally, data analysis on the orthogonal arrays can be easily performed.

3.2.4.3. Application of the Taguchi Method.

The pilot-plant design meant that the number of tests that could be carried out on the apparatus was large. This was due to the number of controllable variables that could be implemented on the pilot-plant and also the numerous levels at which these variables could be set. With the possibility of a potentially exhaustive number of tests that could be carried out within the experimental period, it was important that the experiments were planned in a controlled manner. Planning the experiments in a controlled manner would help to ensure that the overall aims of the study would be met. In order to aid experimental design, the Taguchi design approach was implemented. As previously mentioned the Taguchi method uses orthogonal arrays as a means of statistically planning experiments and analysing the results. Incorporating the Taguchi method into the experimental phase of the project would ensure that the maximum amount of information was gained from the limited number of laboratory tests. The Taguchi method also provides a means for the statistical analysis of the results, therefore the results generated by the Taguchi analysis could be systematically analysed to identify which of the design variables (or combinations of) were likely to produce the most significant positive effect within the process. For the purpose of the study, process optimisation was regarded as maximising the time to component breakthrough. Referring to Section 1.1.4 of Chapter 1, benzene is considered the organic compound to which the drinking water standards are based upon, therefore process optimisation would be considered maximising the time to breakthrough of benzene. It was envisaged that the experimental results would help produce a set of design criteria for a compact remediation unit, optimised for the economic removal of fuel compounds from groundwater.

Literature did not suggest that the Taguchi approach had been applied to experiments similar to those implemented in the fuel oil study. Case studies in literature suggested the Taguchi method had been extensively used in the electronics industry (Dehnad, 1989, Phadke, 1989, Roy, 2001), therefore the study also presented an opportunity to test the Taguchi method in a novel way. Although the experiments were designed using the Taguchi procedure, the results would still enable the comparison of the technologies to be made in the conventional manner by splitting the results into air-stripping and adsorption separately.

The aim of the implementation of the Taguchi method in the design and optimisation of the pilot-plant was summarised as follows;

- To statistically design the pilot-plant experimental phase using orthogonal arrays, where control variables and BTEX/ MTBE influent concentrations were altered accordingly.
- To provide an indication of the optimum process parameters and an indication of the value at which these values should be set.
- To investigate the pilot-plant characteristics with respect to the removal of BTEX and MTBE from solution, where the detection of benzene in the effluent at concentrations >1μg/L was considered breakthrough (presented in time, bed-volume or EBCTs).

Four steps are generally used when implementing the Taguchi method to design experiments. These steps were implemented when designing the experimental phase of the fuel oil study; 1) The problem is formulated, 2) The experiment is planned, 3) The results are analysed and 4) The experiment is confirmed using a verification test. The verification run is formulated upon the analysis of the orthogonal array, where the optimum values suggested by the analysis are run in a final test. If the parameters run in the final test verify the findings of the Taguchi analysis then the variables are adopted for the process design. If the parameters run in the final test do not verify the findings, then the entire experiments are reformulated and the process started again from the beginning.

3.2.4.4. Selecting the Standard Orthogonal Array.

There are 18 standard orthogonal arrays tabulated within the Taguchi method and choosing the most suitable array for the given experiment is an important consideration in the Taguchi method.

Seven variables were identified on the pilot-plant with a view to providing a balance between extending the time to component breakthrough and the economical benefit of keeping parameters such as the air-to-water ratio or the bed depth of the carbon low. These were;

- Influent concentration of BTEX compounds (μg/L).
- Influent concentration of MTBE (μg/L).
- Water flow rate through the air-stripping column (L/min).

- Air flow rate through the air-stripping column (L/min).
- Height of packing within the air-stripping column (mm).
- Bed depth (and hence EBCT) of carbon within adsorption columns (mm).
- Type of carbon used in adsorption columns.

The flow rate of water through the adsorption column was kept constant throughout all tests (1.05L/min).

The noise variables considered when designing the experiments were defined as follows;

- Influent water temperature (°C).
- Influent water pH.
- Influent water conductivity (mv).
- Laboratory temperature (°C).

Given the above experimental variables the L8 orthogonal array table was chosen in order to satisfy the aims of the fuel oil project. The L8 array accommodates seven two-level design variables from 8 experimental runs. The benefit of implementing the two-level L8 array was that seven variables could be tested throughout the experimental period. This was advantageous to the fuel oil project because of the large number of (important) variables that could be tested on the pilot-plant between tests. Table 3.10 details the variables used in the L8 orthogonal array, where 1 and 2 represent the lower and upper values of each design variable respectively.

Taguchi Experiment No.	VARIABLES						
	1	2	3	4	5	6	7
	BTEX Conc. (µg/L)	MTBE Conc. (µg/L)	Q_A (L/min)	Q_W (L/min)	GAC BD (mm)	Packing BD (mm)	Carbon Type
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Table 3.10. L8 Standard Orthogonal Array.

The two-level L8 orthogonal array does have disadvantages over other arrays (for example the three-level L9 orthogonal array), when it comes to the statistical analysis and interpretation of the data. Three-levels for each control factor would detect any non-linear relationships between the factors and the output variables and obtain information over a wider range of variables. However, to implement a three-level orthogonal array using all of the variables required for the pilot-plant experiments, the array would have been too great for the remit of the study. Note that the 'smallest' three-level array (L9) utilises only four three-level variables, over nine experiments.

The limitations of the L8 array are examined in greater detail in Chapter 4.4 of the fuel oil study.

3.2.5. Pilot-Plant Parameters.

Table 3.11 details the pilot-plant variables used within the Taguchi orthogonal array, where BD = Bed Depth.

	VARIABLES						
	1	2	3	4	5	6	7
	BTEX Conc. (µg/L)	MTBE Conc. (µg/L)	Q_A (L/min)	Q_W (L/min)	GAC BD (mm)	Packing BD (mm)	Carbon Type
1	40	5	25	2.1	25	750	F400
2	100	40	180	2.75	50	1500	F600

Table 3.11. Experimental Variables Selected for L8 Orthogonal Array.

3.2.6. Pilot-Plant Procedure.

3.2.6.1. Cleaning the Pilot-Plant Prior to a Run.

Before each experiment was run, the pilot-plant was cleaned to remove traces of organic materials that could carry over to the next test.

The glassware used to hold the concentrate was rinsed three times with deionised water. The aspirator was filled to the top with deionised water for storage purposes.

Wherever possible, all PTFE and peristaltic tubing used on the rig was replaced with new. The two steel tanks were scrubbed, filled with clean water and rinsed. The rig was reset and run with clean water for a period of 48 hours.

3.2.6.2. Operating the Pilot-Plant.

The lid to the top of the adsorption column was removed and the carbon carefully placed into the apparatus using a funnel. The carbon was filled to a pre-determined mark on the column corresponding to the required depth of the sampling ports. For F400 and F600 the approximate mass of carbon required was 2.6 and 3.76kg respectively. This was calculated using the density of each carbon.

The lid to the column was replaced, ensuring a good seal. The valve to the head tank was closed and the backwash effluent valve opened. The water backwash was turned on at a low flow rate, enabling the carbon to become wet with minimal pockets of air. Once all of the carbon had become wet the column was tapped with a wooden hammer to remove any further trapped air. If any air

pockets remained, the backwash was switched off and the bed allowed to settle. The backwash process was then repeated.

Once all the air was removed from the column, the backwash water was then used to remove carbon fines from the bed. The backwash water leaving the carbon column was left to run clear. The backwash water was then switched off and the bed allowed to settle. The column was then tapped with a wooden hammer to position the carbon at the appropriate mark.

The valve from the constant head tank was opened and the water allowed to enter the air-stripping column. The flow rate was controlled from the ball valve and measured volumetrically from the water leaving the air-stripper column.

The lower tank was allowed to fill with water to a level just below the overflow. The peristaltic pump was then switched on and the tank supplying the adsorption column also allowed to fill to a level just below the overflow. Finally the flow meter controlling the adsorption column was set to the required flow rate. Adjustments to the speed of the peristaltic pump were made if necessary to control the overflow rate.

3.2.6.3. Required Dosage Level.

The dosage requirements of BTEX/ MTBE compounds were based on mass balance. Figure 3.15 illustrates the mass balance between the influent water, the dosage tank and the required level of BTEX/ MTBE for the appropriate test.

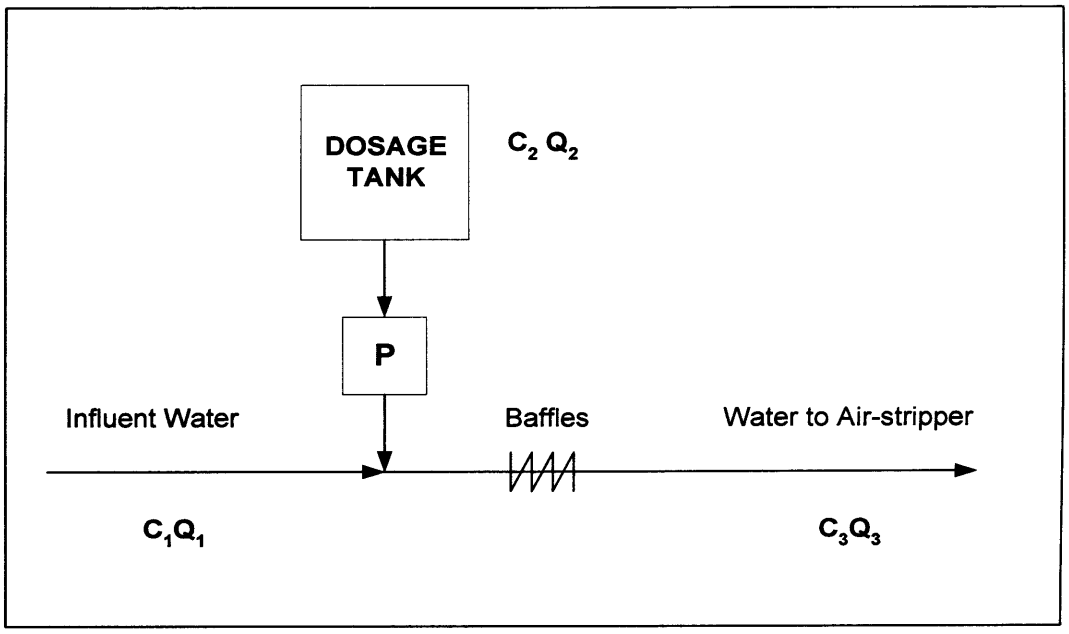


Figure 3.15. Mass Balance Equation for Pilot-Plant Dosing Procedure.

From figure 3.15;

$$C_1Q_1 + C_2Q_2 = C_3Q_3 \qquad \textbf{(eqn 3.4)}$$

Where C_1 = Concentration of BTEX/ MTBE in lab water (μg/L), Q_1 = Flow rate of influent water (L/min), C_2 = Concentration of BTEX/ MTBE solution in dosing tank (μg/L), Q_2 = Flow rate of BTEX/ MTBE solution (L/min), C_3 = Required concentration of BTEX/ MTBE compounds entering the air-stripper (μg/L) and Q_3 = Combined water flow rate (L/min).

Assuming the concentration of BTEX/ MTBE in the influent water = 0μg/L then;

$$C_2Q_2 = C_3(Q_1+Q_2) \qquad \textbf{(eqn 3.5)}$$

The flow rate of the peristaltic pump delivering the concentrate (Q_2) was set at 2.5ml/min for the duration of the experimental phase. The concentration C_3 was dictated by the Taguchi array and the overall flow rate Q_3 was the sum of the influent water flow rate and the flow rate of the BTEX/ MTBE solution. The unknown was therefore the concentration of the BTEX/ MTBE within the dosing tank (C_2). By rearranging the equation;

$$C_2 = \frac{(Q_1 + Q_2)C_3}{Q_2} \qquad \textbf{(eqn 3.6)}$$

For example experiment number 1 - C_3 (benzene) = 100μg/L, Q_1 = 2.1L/min, Q_2 = 2.5×10^{-3} L/min, therefore;

$$C_2 = \frac{(2100+2.5)100}{2.5} = 84100\mu g/L = 84.1mg/L \qquad \textbf{(eqn 3.7)}$$

Required mass of benzene required for 9.8L storage vessel;

$$84.1mg/L \times 9.8L = 824.1mg = 0.824g \qquad \textbf{(eqn 3.8)}$$

It was important that all the compounds dissolved in the dosing tank. The effect of co-solvency was taken into account when considering whether the BTEX/ MTBE compounds would dissolve in the dosing tank. The solubility of a compound within a mixture will be less than that within a pure compound-water mixture. As detailed in Section 1.3.4.2 of Chapter 1, within a mixture the concentration of each compound within the water is equal to its mole fraction in the mixture multiplied by its specific solubility. As the number of moles of each individual compound added to the dosing tank was very low and the number of moles of water (also included in the mixture) was very high, the impact co-solvency was considered in this case to be minimal.

3.2.6.4. Preparation of Concentrate.

Appropriate concentrates of MTBE and BTEX were made up. Individual neat analytical grade BTEX and MTBE compounds were purchased from Fisher Scientific and stored within a locked steel cabinet. NB, all three xylene isomers were used in the experiments (ortho, meta and para).

Within the fume cupboard the 10L aspirator was filled with deionised water to the 9L mark. A clean 50ml volumetric flask was partly filled with deionised water and placed within the balance and then zeroed. The first of the BTEX/ MTBE compounds were transferred to volumetric flask using a glass pipette and the correct amount accurately weighed. The glass pipette was then discarded in an organic contamination jar, which was emptied periodically for incineration. The glass stopper was put into place on the volumetric flask and inverted to mix the solution. The method was repeated for the rest of the compounds. The process was carried out as quickly as possible in order to reduce the amount of material lost to the atmosphere.

Once all the compounds had been measured out, the content of the volumetric flask was transferred to the aspirator and made up to the 9.8L mark with deionised water. The adapted rubber/ PTFE bung was replaced and the dosage equipment carried to the pilot-plant, where it was placed upon the magnetic stirrer. The Fluorel tubing was attached and the equipment left to equilibrate for a period of 1 hour before the in-line dosing pump was switched on.

Once the pilot-plant had been set up and the dosage equipment put into place, the peristaltic pump feeding the concentrate was switched on and the test commenced.

3.2.6.5. Sampling Procedure.

Figure 3.16 illustrates the sample points used on the pilot-plant.

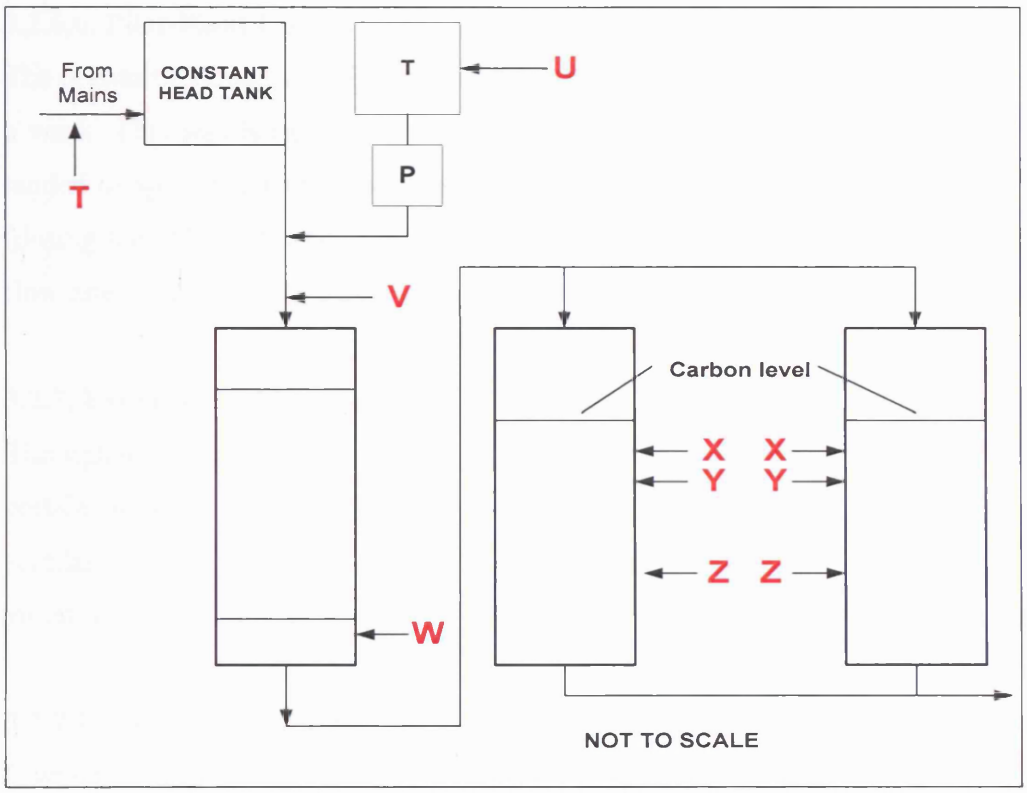


Figure 3.16. Pilot-Plant Sampling Ports.

For the period of each experimental run, samples were generally taken every Monday, Wednesday and Friday. Sampling port T represents the influent water to the pilot-plant and was used to monitor the quality of the water for background BTEX and MTBE levels. Sampling port U represents the fuel concentrate within the dosing tank. Sample ports T and U were only monitored intermittently. Sampling ports X, Y and Z represent the 25, 50 and 175mm GAC bed depths respectively. Two sets of samples V, W, X, Y and Z were taken three times per week, one actual and one repeat. A repeat sample was taken to ensure that there were samples available to run on the GC-MS in the event of a malfunction.

Clean 40ml vials were used to collect the samples. Water was allowed to run through each sample port for a period of 1 minute before test was taken. This was to ensure the samples taken were directly from the pilot-plant, rather than stagnant water from within the sampling pipes.

Sampling was carried out as quickly as possible in order to reduce the amount of VOCs lost to the atmosphere. The samples were individually bagged and placed immediately into the fridge until the time when they were run on the GC-MS. The exact timing of each sample taken was recorded.

3.2.6.6. Pilot-Plant Checks.

The peristaltic tubing used in pump 2 (feeding the head tank) was changed twice a week. This was because the high flow rates required by the pump the tubing tended to split if not replaced regularly. The peristaltic tubing used in pump 1 (dosing the BTEX/ MTBE mix) was changed if signs of splitting appeared. All flow rates were checked daily.

3.2.7. Experimental Errors.

Throughout the design of the pilot-plant and the experimental work-plan a certain amount of error was expected. The design of the apparatus and the standardisation of the pilot-plant procedure were both designed to minimise this variation. An estimation of the experimental error is included in Chapter 4.1.

3.2.7.1. Variation in Influent.

It was expected that the influent would vary throughout each run. The variation in the influent concentration can be observed in similar laboratory-scale studies throughout literature (e.g. Hand *et al*, 1989). It follows that the physical properties of MTBE and BTEX compounds (e.g. volatility, solubility and adsorption) would cause some variation in the influent.

A standard MTBE/ BTEX preparation procedure was implemented (Section 3.2.6.4). This procedure was designed to minimise variation in the concentrate preparation and was applied both intra-test and inter-test. It was assumed that operator error would be same throughout all tests.

The greatest contribution to a variable influent is most likely be caused by the storage and delivery apparatus to the pilot plant. Given that a method needed to be implemented that could be left unsupervised for a minimum of 3-days, or without further addition of fuel concentrate, the aspirator method was deemed the most practical solution. Other delivery methods for example syringe pumps were investigated, but were found not to be suitable for use within the pilot-plant. In the case of the syringe pump, the MTBE – BTEX concentration that would be required within the syringe was calculated to be higher than the solubility of each compound.

Although BTEX compounds are known to be water soluble, it was envisaged that problems would occur when trying to get the compounds to completely dissolve

in the dosage tank. This in-turn would affect the influent concentration. The addition of a solvent such as methanol to the MTBE - BTEX solution was considered, which would have ensured that the compounds dissolved fully within the solution. However, this was deemed unsuitable as it would affect the processes being tested (for example adsorption).

Within the course of an experiment, it is likely that the concentration of MTBE and BTEX will reduce with time as the level of the concentrate falls. VOCs will effectively be lost to headspace of the aspirator. This also is likely to cause variations in the influent concentration. If the concentration of MTBE – BTEX within the aspirator could be quantified throughout each experiment, it is likely that concentrations will be at their highest immediately after the aspirator has been filled, with concentrations decreasing over time until the vessel is filled.

Wherever possible, non BTEX – MTBE adsorbing materials were used in the construction of the pilot-plant. However throughout the experiments, free-phase MTBE and BTEX compounds were observed 'sticking' to the hose used to drain the concentrate within the aspirator (figure 3.12).

The sampling procedure was standardised throughout the experimental period. Samples would be taken in the same way throughout each experiment. However, the method was not entirely suitable as it is likely that some VOCs would be lost to the atmosphere during the filling of the vials. This may cause variation in the 'true' sample concentrations.

Whenever possible, repeat samples will be taken and run on GC-MS alongside the other samples. Comparing 2 sets of samples will help quantify experimental errors.

3.2.7.2. Storage of the Samples.

Due to the fact that the GC-MS resource was only available at the end of the 4-week test run period, the samples taken throughout the experimental period had to be stored. It was known that the storage of samples was not ideal, as the samples may be subjected to chemical or biological breakdown throughout the storage period.

In order to minimise the effect of storage until a time when the GC-MS resource became available, the samples were individually bagged and stored in a fridge free of all other substances. Samples were run on the GC-MS as soon as possible.

From literature it is known that MTBE does not readily degrade and that BTEX compounds are more readily degradable. It would follow that if sample degradation was to occur, BTEX would be more affected than MTBE.
Errors in the GC-MS method are presented in Section 3.3.4 (RSD% values).

3.2.8. Pilot-Plant Experimental Work Plan and Conditions.

Table 3.12 presents the pilot-plant experimental chronology, whilst Table 3.13 (A and B) detail the experimental work-plan for the pilot-plant. Note that the concentration of BTEX and the amount of BTEX added to the aspirator (Table 3.13A) refers to the concentration and mass of each individual BTEX compound. That is the total concentration of BTEX is 600μg/L.
Throughout Chapter 4, experiment numbers can be identified using the following tables.

Experiment No.	Equivalent Taguchi Run	Experimental Period	No. of Days	GC-MS Analysis
Pre-Test	-	14/11/01-05/12/01	21	05/12/01
1	7	23/01/02-13/02/02	21	12/02/02
2	1	28/02/02- 26/03/02	26	25/03/02
3	3	23/07/02- 14/08/02	21	12/08/02
4	8	27/08/02- 17/09/02	21	16/09/02
5	4	07/10/02- 28/10/02	21	28/10/02
6	6	07/01/03- 28/01/03	21	27/01/03
7	2	03/02/03- 24/02/03	21	16/05/03
8	5	25/02/03- 18/03/03	21	15/05/03
11	V	29/05/03-19/06/03	21	18/06/03
Detailed below are tests also run throughout the experimental period that were not included in the experimental results				
-	4	13/05/02- 07/06/02	26	17/06/02 Failed due to GC Fault
-	5	12/11/02- 02/12/02	21	02/12/02 Failed to due GC Fault

Table 3.12. Pilot-Plant Experimental Chronology.

Experiment No.	Equivalent Taguchi Run	BTEX Conc (ug/L)		MTBE Conc (ug/L)		Wt. Added to 9.8L	
		Target	Actual (Average)	Target	Actual (Average)	BTEX	MTBE
Pre-Test	-	100	-	40		0.82	0.33
1	7	100	135	40	175	0.82	0.33
2	1	40	74	5	23	0.33	0.041
3	3	40	28	40	67	0.33	0.33
4	8	100	164	40	163	1.1	0.43
5	4	40	30	40	53	0.43	0.43
6	6	100	51	5	11	1.1	0.054
7	2	40	NDA	5	6	0.43	0.054
8	5	100	NDA	5	13	0.83	0.041
V	V	100	91	5	10	0.83	0.041

Table 3.13 A. Pilot-Plant Experimental Work-Plan.

Experiment No.	Equivalent Taguchi Run	Air-flow Rate (L/min)	Water-flow Rate (L/min)	Effective Air-to-Water Ratio	GAC Bed Depth (mm)	Packing Bed Depth (mm)	Carbon Type
Pre-Test	-	25	2.1	12	50	1500	F400
1	7	25	2.1	12	50	1500	F400
2	1	25	2.1	12	25	750	F400
3	3	180	2.1	86	25	1500	F600
4	8	25	2.75	9	25	750	F600
5	4	180	2.75	65	50	750	F400
6	6	180	2.75	65	25	1500	F400
7	2	25	2.75	9	50	1500	F600
8	5	180	2.1	86	50	750	F600
8 Repeat	V	180	2.1	86	50	750	F600

Table 3.13 B. Pilot-Plant Experimental Work-Plan.

3.3. GC-MS Procedure.

Section 3.3 details the GC-MS method used throughout the whole of the experimental work. The method was developed specifically for the needs of the project. The method can be considered; the simultaneous high throughput quantitative analysis of BTEX/ MTBE compounds, using a Precept II autosampler and Tekmar 3000 P&T system linked to a Fisons 8000 Series gas chromatograph. The GC was in turn interfaced to a MD 800 quadrupole mass spectrometer.

The section follows the development of the GC-MS method from the RSSCT pre-test through to the pilot-plant experiments. Changes to the method are detailed, along with details of new additions to the GC-MS set-up.

Section 3.3.4 presents the GC-MS validation procedure and associated errors.

General Laboratory Practices.

Care was taken throughout the work undertaken in the Wolfsen Lab to avoid organic contamination of samples and standards. Cross contamination of samples and standards was particularly relevant because of the low concentrations of compounds being analysed (<1μg/L). In general, all work was carried out in an organic free environment and all glassware used was cleaned to the required standard. Ultra pure water was used for both lab blanks and making standards.

Deionised Water.

Two types of water purifiers were used in the lab;

An Elga Option 3 Water Purifier provided deionised water. Deionised was used throughout the GC procedure to wash vials and caps.

An Elga Maxima Ultra Pure water system was used to produce ultra pure water. The system took water from the deioniser and subjected it to UV light. Ultra pure water was also used for vial cleaning purposes. It was also used for lab blanks and for making standards.

40ml Glass Vial/ Vial-Cap Cleaning Procedure.

All 40ml vials and vial caps used to collect samples and make the standards were cleaned according to USEPA Protocol B (all USEPA methods can be downloaded from their web site - www.epa.gov). The 40ml vials were

compatible with the autosampler. The TOP Hat Closures (vial caps) used throughout the experimental procedure met USEPA requirements for the analysis of VOCs.

The vial caps and associated liners were separated and placed in glass dishes. The dishes were filled with deionised water and Decon 90 cleaning agent added. Decon 90 is a lab grade, biodegradable, non-phosphate detergent used to remove organics from glassware. The 40ml vials were placed into a large glass beaker and filled with deionised water and Decon 90. All vials and vial caps were soaked for 24 hours and then each rinsed 3 times with deionised water and 3 times with ultra pure water. They were then oven dried overnight and assembled in an organic free environment.

Volumetric Flask Cleaning Procedure.

All volumetric flasks used for making standards were rinsed 3 times with deionised water and 3 times with ultra pure water. They were then filled to the top with ultra pure water, and the caps replaced for storage purposes.

3.3.1. GC-MS Method.

Background to P&T GC-MS Method.

The GC-MS method used throughout the experimental phase of the project was based upon two commonly accepted methods; USEPA method 524.2 and the comparable US Geological Survey (USGS) method for MTBE and other Fuel Oxygenates. Both methods can be accessed from the relevant websites;

- <www.epa.gov>
- <www.usgs.gov>

Procedures such as the USEPA method 524.2 were introduced to standardise the testing of a variety of mediums (including drinking water) within the US and provide guidelines for individuals and relevant companies.

Complicated aqueous mixtures containing volatile BTEX and MTBE compounds requires an effective system to concentrate the samples for gas chromatography. Two systems enable the compounds to be concentrated prior to injection into the column, either purge and trap (P&T) or headspace analysis. As discussed previously, P&T GC-MS was used throughout the investigation.

The P&T technique has been successfully applied to the analysis of trace volatile components in environmental samples. USEPA method 524.2 provides the analysis of approximately 60 aqueous compounds (including all BTEX and MTBE compounds) using full-scan GC-MS. A known volume of sample (either 5 or 25ml) is purged with an inert gas such as helium or nitrogen. The analytes are then swept out of the aqueous solution as gases and are then concentrated on the sorbent bed (trap). The trap is coupled directly to the GC. The analytes are then thermally desorbed onto the column using a pre-determined heating program. Once on the column standard GC separation takes place, followed by detection, quantification and conformation using mass spectrometry.

Parameters affecting the efficiency of P&T sample concentration include; time and temperature for sample purge, moisture control, desorption of trapped volatile organics and trap baking. The narrow bore chromatography column as used throughout the experimental period, allows the efficient separation of the analytes even with shorter analysis times and oven temperatures.

In order to automate the process, the P&T was directly coupled to a compatible autosampler.

GC-MS Method Version 1.

The following section details the GC-MS method used for the RSSCT pre-test. Changes made to the method in order to increase its sensitivity will be detailed in later sections. The section also includes the procedure for making standards.

The MS parameters were set as follows; ionisation voltage 70eV, source temperature 300°C, interface temperature 250°C. Separation was performed using a SGE fused silica capillary column, 20m × 0.32 mm (internal diameter), coated (0.5μm) with 5% phenylpolysilicone (BP5).

A PC running the Masslab program controlled all elements of the GC-MS. Masslab also provided the means for qualitative and quantitative chromatogram peak analysis.

Helium was used as carrier gas with a head pressure of 110 kPa. Initial oven temperature for the analytes was 30°C for 4 minutes, which was then ramped at 8 °C/min to 160°C.

5ml of each sample was purged for 10 minutes and then desorbed for 5 minutes at 250°C from a VOCARB 3000 (K) purge trap. The sample was then swept onto the GC column via a transfer line held at 130°C.

The trap was preconditioned before use at 270°C for 60 minutes and was baked after each sample at 260°C for 6 minutes.

GC-MS Pre-checks.

A series of checks were carried out before each GC-MS run commenced in order to ensure the machine was in peak working condition. Peak working condition of the GC-MS was vital to ensure good chromatography. The system was first checked for leaks. Leaks could occur any where along the gas line from the helium cylinder through the end of the GC column entering the MS interface. Leaks would show up on the MS detector as peaks showing high concentrations of nitrogen and water. If leaks occurred, the line was tested until the leak was found. Only when the nitrogen and water peaks resided was the run allowed to commence.

Standards.

EPA Method 524.2 VOC Mix and Rev 4 Update Mix (both containing 200ug/L of each compound) were used to make up the calibration standards. Supelco supplied both VOC standards; EPA Method 524.2 VOC Mix CAT No. 47932 and Rev 4 Update Mix CAT No. 506524. The VOC mix contained 60 analytes in methanol including all BTEX compounds. The Rev 4 Update contained 18 analytes in methanol including MTBE.

The 1ml VOC Mix vial was snapped opened and the solution transferred to a second 1ml glass vial using a glass pipette. A septum cap was placed onto the 1ml vial immediately in order to reduce the amount of standard lost to the atmosphere. This was repeated for the Rev 4 Update Mix. The pipette and empty vials were discarded for incineration.

SGE gas-tight syringes were used to make up each standard. Methanol was used to remove trace organic compounds from the glass syringes. The syringes were rinsed three times before and after each standard preparation with methanol.

A clean 10ml septum vial was partly filled with ultra pure water. A stock solution of 2µg/ml was prepared by syringing 100µl of each standard into the 10ml vial. Care was taken when piercing the septum, so not to bend the syringe needle. Air bubbles were prevented from entering the syringe by carefully inverting the apparatus whilst drawing in the solution. The 10ml vial was then immediately made up to the mark with ultra pure water and the cap fixed into place.

Dilutions of the stock solutions were made using volumetric flasks. The volumetric flasks were partly filled with ultra pure water. The appropriate amount of stock solution was transferred to the volumetric flasks, which were then made up to the mark with ultra pure water. The solution was then transferred immediately to 40ml vials. Table 3.14 details the quantity of stock solution used to produce the required standard.

Desired Conc. (µg/L)	Volumetric flask used (ml)	Amount of stock solution. added (µl)
1	100	50
1	200	100
10	100	500
10	200	1000
15	100	750
15	200	1500
20	100	1000
20	200	2000

Table 3.14. Standard Preparation.

Two sets of 40ml standards (1, 10, 15 and 20µg/L) were made for each batch of samples run on the GC-MS. One set was placed before the samples, and the other set placed after. This meant that the sensitivity of the GC-MS could be monitored throughout the run.

In addition to this, two extra 20µg/L standards (termed drift standards) were made up for each batch of samples and placed throughout each run. The drift standards were used to monitor the sensitivity of the GC-MS throughout the run.

Adjustments to the GC could then be made if the performance of the GC altered throughout the run.

If required, the standards were individually sealed in polythene bags and stored in the fridge until needed. However, standards were stored for the period of the immediate GC-MS analysis only. Fresh standards were made up at the beginning of each run.

GC-MS Method Version 2.

The GC program was altered for the RSSCT Run 1 onwards, in order to improve the sensitivity of the method. Helium was used as the carrier gas with a head pressure of 110 kPa. Initial oven temperature for the analytes was 30°C for 5 minutes, which was then ramped at 10°C/min to 100°C and then ramped at 20° C/min to 200°C.

GC-MS Method Version 3.

The GC program was altered from Taguchi run 3 onwards, to provide easier identification and quantification of ethylbenzene, MP-xylene and O-xylene compounds. The program was also altered so the oven did not have to cool to 30°C before the samples were swept onto the column. This reduced the analysis time per sample.

Helium was used as the carrier gas with a head pressure of 110 kPa. Initial oven temperature for the analytes was 40°C for 6 minutes, which was then ramped at 6.7°C/min to 100°C, and then ramped at 30°C/min to 200°C, which was held for 1 minute.

GC-MS method version 3 was used throughout the rest of the experimental plan.

GC-MS Modifications.

Change of Column.

A Thames Restek column RTX5 - MS (30m length, 0.32μm column diameter, 0.5μm phase) was purchased and installed to provide the analysis for RSSCT Run 1 onwards. The RTX5 - MS column was specific to the needs of the project. The column was conditioned before work on the GC-MS commenced, by heating the column on a preset GC program.

Addition of 25ml Purge Glassware.

A 25ml purger was installed for RSSCT Run 2. The greater the amount of sample purged the more sample will be swept onto the column, hence the greater the sensitivity of the method. The 25ml glassware was used for the remainder of the GC-MS analysis.

20ml of each sample was purged for 10 minutes and then desorbed for 5 minutes at 250°C from the VOCARB 3000 K purge trap. The sample was then swept onto the GC column via a transfer line held at 130°C.

Change of Standards.

From Run 2 onwards, a hydrocarbon (HC) BTEX/MTBE mix standard (2000µg/L of each compound) was used for quantification purposes. This replaced EPA Method 524.2 VOC Mix and Rev 4 Update Mix.

The HC BTEX/MTBE standard was supplied by Supelco (CAT No. 47505-U). Only BTEX and MTBE compounds were present in the mix (in methanol), making the quantification of the standards easier.

10µl of the standard was made up to 10ml producing stock solutions of 2µg/L. Standards were then made in the same manner detailed previously in this section.

Replacement Parts.

A number of replacement parts were required to maintain the GC-MS throughout the experimental period. This ensured the GC-MS was in peak working condition for all runs. The new parts included; a new valve for auto-sampler, a new syringe for auto-sampler and a new pressure control valve for the P&T system. Other routine maintenance such as the cleaning of the MS source also ensured the GC-MS was in peak working condition.

3.3.2. Analysis of Diesel.

For background information purposes a neat diesel sample was run on the GC-MS. The sample was injected directly into the GC oven. A typical diesel chromatogram was produced and can be found in the literature review (Figure 1.7.). Helium was used as the carrier gas with a head pressure of 110 kPa. Initial oven temperature for the analytes was 30°C for 5 minutes, which was then

ramped at 15°C/min to 200°C and held for 5 minutes. It was then ramped at 20° C/min to 320°C. The MS was set to analyse from 45-500 MZ, where M represents the molecular weight of the compounds and Z represents the charge of the compound. The program carried a solvent delay time of 4 minutes.

3.3.3. Qualitative and Quantitative Peak Analysis.

Each chromatogram generated by the GC-MS was qualitatively and quantitatively analysed for BTEX and MTBE compounds individually. Analysis was carried out on all standards, samples and lab blanks. Identification of each peak was carried out using the retention times of the compound and the application of mass spectrometry tool on the Masslab program. Although Masslab had the provision for programmed quantitative and qualitative analysis of the samples without any user input, all analysis was carried out manually by identifying each peak, integrating the peak area and finally transposing the data into calibration curves and data analysis spreadsheets. The manual method of qualitative and quantitative analysis was time consuming but presented an opportunity to ensure all analysis was carried out to a high standard.

As previously stated, the BTEX and MTBE peaks were identified on each chromatogram using retention times and the mass spectrum graphs generated by the mass spectrometer. Masslab provided an extensive library of mass spectrum graphs for individual compounds, enabling exact matches for each peak. From the information provided with the standards, it was known that MTBE would be the first compound to elute - followed by benzene, toluene and ethylbenzene. Next to elute was M- and P-xylene, which eluted at the same time. The final peak on the chromatogram was O-xylene. Example chromatograms can be seen in section 3.3.4.

Integration of each peak was carried out using the integration tool on the Masslab program. Integration was carried out by the same user for the entire experimental period, ensuring possible user error was carried over to each period of analysis. Straight-line calibration graphs were produced from the integration of peaks generated from the range of standards.

A spreadsheet was developed where the concentration of each sample was calculated from each calibration graph using the following equation;

$$y = mx + c \qquad \textbf{(eqn 3.9)}$$

Where y = peak integration value (unitless), x = concentration (μg/L), m = gradient of the straight-line graph and c = y intercept of the straight-line graph. The gradient and intercept were calculated using the appropriate function within MS Excel. For each sample, x (the concentration of the sample) was unknown, therefore equation X was rearranged to form;

$$x = \frac{y - c}{m} \qquad \textbf{(eqn 3.10)}$$

Equation 3.14 was inputted into an Excel spreadsheet where each x value was calculated automatically within the program.

Example: Run 5.

Tables 3.15 and 3.16 present the spreadsheets for MTBE and benzene, throughout Run 5.

X-Axis Integrated Area	Y-Axis Conc. (µg /L)	Sample ID	Sample Type	Integrated Area	Concentration (µg /L)	Sample Conc. (µg /L)
0	0	s614	V	$5.4x10^{+07}$	15	150
6.2E+06	1	s615	W	$3.9x10^{+07}$	11	107
5.1E+07	10	s616	X	$3.9x10^{+07}$	11	107
6.3E+07	15	s617	Y	$3.4x10^{+07}$	9.2	92
7.3E+07	20	s618	Z	$1.9x10^{+07}$	4.9	49
0	0	s619	V	$4.2x10^{+07}$	11	114
3.8E+06	1	s620	W	$2.9x10^{+07}$	7.8	78
3.4E+07	10	s621	X	$3.3x10^{+07}$	8.7	87
4.9E+07	15	s622	Y	$2.9x10^{+07}$	7.8	78
6.3E+07	20	s623	Z	$2.2x10^{+07}$	5.6	56
		s624	20	$7.0x10^{+07}$	20	20
		s625	V	$5.8x10^{+07}$	16	162
Correlation	0.97	s626	W	$5.0x10^{+07}$	14	136
		s627	X	$4.2x10^{+07}$	11	115
Slope	$3.5x10^{+06}$	s628	Y	$3.7x10^{+07}$	10	100
		s629	Z	$2.7x10^{+07}$	7.1	71
Intercept	$2.3x10^{+06}$	s630	V	$6.5x10^{+07}$	18	182
		s631	W	$5.0x10^{+07}$	14	137
		s632	X	$4.4x10^{+07}$	12	120
		s633	Y	$3.9x10^{+07}$	11	107
		s634	Z	$3.3x10^{+06}$	7.5	75
		s635	20	$7.0x10^{+07}$	19	19
		s636	V	$4.8x10^{+07}$	11	107
		s637	W	$4.7x10^{+07}$	5.8	58
		s638	X	$4.2x10^{+07}$	5.7	57
		s639	Y	$4.1x10^{+07}$	6.3	63
		s640	Z	$3.4x10^{+07}$	6.7	67
		s641	V	$3.9x10^{+07}$	21	210
		s642	W	$2.2x10^{+07}$	16	158
		s643	X	$2.2x10^{+07}$	12.5	125
		s644	Y	$2.4x10^{+07}$	11	114
		s645	Z	$2.5x10^{+07}$	10	105

Table 3.15. Quantification Spreadsheet for MTBE.

X-Axis Integrated Area	Y-Axis Conc. (µg /L)	Sample ID	Sample Type	Integrated Area	Concentration (µg /L)	Sample Conc. (µg /L)
0	0	s614	V	$1.2x10^{+08}$	10	102
1.6E+07	1	s615	W	$2.8x10^{+07}$	2.3	23
1.5E+08	10	s616	X	$1.1x10^{+07}$	0.9	8.5
2.1E+08	15	s617	Y	$2.9x10^{+06}$	0.1	1.2
2.7E+08	20	s618	Z	0.00	<1	<1
0	0	s619	V	$8.4x10^{+07}$	7.2	72
6.9E+06	1	s620	W	$2.3x10^{+07}$	1.9	19
9.4E+07	10	s621	X	$9.6x10^{+06}$	0.7	7.1
1.4E+08	15	s622	Y	$2.6x10^{+06}$	<1	<1
1.9E+08	20	s623	Z	0.00	<1	<1
		s624	20	$2.2x10^{+08}$	19	19
		s625	V	$7.7x10^{+07}$	6.6	66
Correlation	0.95	s626	W	$2.1x10^{+07}$	1.7	17
		s627	X	$1.4x10^{+07}$	1.1	11
Slope	$1.1x10^{+07}$	s628	Y	$5.3x10^{+06}$	0.3	3.3
		s629	Z	0.00	<1	<1
Intercept	$1.5x10^{+06}$	s630	V	$1.6x10^{+08}$	14	139
		s631	W	$3.6x10^{+07}$	3.0	30
		s632	X	$2.3x10^{+07}$	1.9	19
		s633	Y	$1.0x10^{+07}$	0.8	7.5
		s634	Z	0.00	<1	<1
		s635	20	$2.1x10^{+08}$	19	19
		s636	V	$1.1x10^{+08}$	8.0	80
		s637	W	$3.8x10^{+07}$	1.8	18
		s638	X	$2.4x10^{+07}$	1.4	14
		s639	Y	$1.0x10^{+07}$	0.8	7.6
		s640	Z	0.00	<1	<1
		s641	V	$9.3x10^{+07}$	17.6	176
		s642	W	$2.2x10^{+07}$	0.5	46
		s643	X	$1.8x10^{+07}$	2.7	27
		s644	Y	$1.0x10^{+07}$	1.6	16
		s645	Z	$3.1x10^{+05}$	0.2	1.8

Table 3.16. Quantification Spreadsheet for Benzene.

Lab blanks were placed within the GC-MS run to monitor possible carry over of BTEX/ MTBE compounds. If BTEX or MTBE compounds were detected within the blanks, the level was subtracted from the values of the samples.

3.3.4. GC-MS Procedure Validation.

The following section presents the GC-MS procedure developed and implemented throughout the experimental period of the study. Comparisons to other P&T GC-MS methods are made using method validity calculations. The results of the validity calculations were also used to express the data presented throughout Chapter 4 of the study. Finally, areas where problems were encountered with the developed method are highlighted within this section.

As discussed in section 3.3, the method adopted throughout the experimental period of the study was specifically designed for the purpose of the fuel oil contamination project. The method was defined as; the simultaneous high throughput quantitative analysis of BTEX/ MTBE compounds, using a Precept II autosampler and Tekmar 3000 P&T system linked to a Fisons 8000 Series gas chromatograph and MD 800 quadrupole mass spectrometer.

Samuel Hall and Sarah Houghton carried out the method development and GC-MS analysis at the Wolfson Laboratory of Geochemistry (UCL).

There are a number of valid GC-MS methods available for the quantification of MTBE and BTEX compounds using P&T. The GC-MS method used throughout the experimental phase was based upon two commonly accepted methods; USEPA method 524.2 and the US Geological Survey (USGS) method for quantification of MTBE and other Fuel Oxygenates. A similar method developed by Bianchi *et al*, 2002 was also researched, which looked at validating a method for the quantification of MTBE, TBA and BTEX compounds from groundwater at trace levels using P&T GC-MS. Limit of Detection (LOD) values using this method ranged from 2.6 to 23 ng/L. The validation procedures used in the method developed by Bianchi *et al*, 2002 were applied to the fuel oil study.

Although the USEPA, USGS and Bianchi method are similar to the method developed for the fuel oil study, the approaches differed in a number of ways;

1) The method developed for the fuel oil study required a high throughput of samples throughout the entire experimental period.
2) An automated approach whereby the system could be set up and left to test all the samples with minimum user input was required. This would allow other work to be carried out at the same time. For this reason a Precept II autosampler was fully integrated into the procedure in order to reduce the experimental effort.

3) Quantification of MTBE and BTEX to trace levels was not required. Referring to Section 2.1 & 2.2 of Chapter 2, quantification of MTBE and BTEX compounds to 1μg/L was required for the study.

Problems Occurred with the Quantification of TEX Compounds.

Problems were encountered with the GC-MS method in the quantification of TEX compounds. For this reason the results for TEX compounds were omitted from the results of the project.

The problems were caused by the irregular peak shapes of TEX compounds on the chromatogram and interference from disinfection by-products (DBPs). DBPs from the laboratory tap water were found to elute at the same time as TEX. These interferences are presented in Appendix C.

The results and discussion section details MTBE and benzene only. This was viewed as an acceptable change to the study due to the fact that the aim of the study was to design a remediation process for the removal of MTBE and benzene. Although TEX compounds were not presented throughout the results chapter or used to formulate the discussion/ conclusion chapter, the compounds were added to the fuel oil concentrate throughout the entire experimental phase. Removing TEX compounds from the fuel concentrate part way through the experimental phase would have altered the characteristics of the influent water.

Method Validity.

The validation process was carried out to EURACHEM guidelines. EURACHEM provides a network of analytical chemistry related organisations in Europe. One of the objective of EURACHEM is the promotion of quality analytical practices. The guidelines used throughout the validation procedure entitled 'The Fitness for Purpose of Analytical Methods: A laboratory Guide to Method Validation and Related Topics' (1998) is available for down load at: www.eurachem.ul.pt/guides/valid.pdf

Four methods of validity were used;

1) LOD (limit of detection). LOD is sometimes referred to as Lower Limit Detection (LLD).
2) LOQ (limit of quantification).

3) Intra-day repeatability using relative standard deviation (RSD)% values on two standard concentration values.
4) Linearity of the calibration curve for 1 - 20µg/L standards (for MTBE and BTEX compounds).

Calculation of LOD.

$LOD = x_b + 2ts_b$ **(eqn 3.11)**

Where x_b = Mean concentration of multiple blank determinations during one GC-MS run (µg/L), t = Constant of the t-student distribution (one-tailed) at 95% confidence and defined degrees of freedom and s_b = Standard deviation of the blank responses (µg/L). t values for the calculation of LOD were sourced from Skoog (1994).

Calculation of LOQ.

$LOQ = x_b + 10s_b$ **(eqn 3.12)**

Where x_b = Mean concentration of multiple blank determinations during one GC-MS run (µg/L) and s_b = Standard deviation of the blank responses (µg/L).

Using the data from Run 8 Repeat the LOD and LOQ values were calculated for MTBE and BTEX compounds.

Table 3.17 details the calculated LOD and LOQ values for the GC-MS method. Values of LOD and LOQ are expressed in µg/L.

MTBE	Conc.(µg/L)		Benzene	Conc. (µg/L)	
	Blank 1	0.60		Blank 1	0.57
	Blank 2	0.60		Blank 2	0.55
	Blank 3	0.62		Blank 3	0.60
	Blank 4	0.63		Blank 4	0.58
	MEAN	0.61		MEAN	0.58
	STEVA	0.02		STEVA	0.02
	LOD	**0.73**		**LOD**	**0.71**
	LOQ	**0.79**		**LOQ**	**0.79**
Toluene	Conc. (µg/L)		Ethylbenzene	Conc. (µg/L)	
	Blank 1	0.76		Blank 1	0.70
	Blank 2	0.71		Blank 2	0.61
	Blank 3	0.82		Blank 3	0.60
	Blank 4	0.83		Blank 4	0.45
	MEAN	0.78		MEAN	0.59
	STEVA	0.05		STEVA	0.10
	LOD	**1.12**		**LOD**	**1.24**
	LOQ	**1.32**		**LOQ**	**1.60**
MP-Xylene	Conc. (µg/L)		O-Xylene	Conc. (µg/L)	
	Blank 1	0.56		Blank 1	0.45
	Blank 2	0.43		Blank 2	0.28
	Blank 3	0.42		Blank 3	0.29
	Blank 4	0.00		Blank 4	0.00
	MEAN	0.35		MEAN	0.25
	STEVA	0.24		STEVA	0.19
	LOD	**1.90**		**LOD**	**1.44**
	LOQ	**2.78**		**LOQ**	**2.11**

Table 3.17. LOD and LOQ Values for MTBE and BTEX Compounds.

From table 3.17 it can be seen that the LOD and LOQ values for MTBE and benzene fall below the 1µg/L concentration level. This means that concentrations of 1µg/L and above expressed in Chapters 4 and 5 of the study were within the detection and quantification limits of the GC-MS method. Although the LOD and LOQ values for MTBE and benzene allow the expression of data to values of 0.8µg/L or above, in order to include a margin of safety all data below 1µg/L was expressed as <1µg/L.

As discussed earlier, problems occurred when quantifying the chromatogram peaks for TEX compounds. This was due to the irregular peak shapes and the

interference from DBPs. The problems associated with the quantification of TEX compounds has been highlighted using the LOD and LOQ calculations and can be observed throughout table 3.16. It can be noted that the LOD and LOQ values for TEX compounds were calculated to be above the values calculated for MTBE and benzene.

Intra-day Repeatability using RSD(%) Values.

Intra-day (or intra-experimental) RSD% values were calculated for the lower and upper end of the calibration curve (1 and 20μg/L respectively). RSD% values are designed to give an indication of the performance of the GC-MS throughout a specific run. The lower the RSD% the better the performance of the GC-MS.

The RSD% calculations made in this section have been utilised along with an estimation of the pilot-plant experimental error, to express the results of the fuel oil study. This is detailed in Chapter 4.1.

Table 3.18 details the RSD% values for MTBE and BTEX compounds.

MTBE	Required Conc.(µg/L)		Benzene	Required Conc.(µg/L)	
	1.00	20.00		1.00	20.00
	Experimental Conc.			Experimental Conc.	
	1.07	19.67		0.95	20.54
	0.99	19.61		1.00	20.02
	0.98	19.41		0.95	20.47
	0.98	20.81		0.90	20.17
	1.14	20.03		1.18	20.94
MEAN	1.03	19.90	MEAN	0.99	20.43
STDEVA	0.04	0.63	STDEVA	0.04	0.25
RSD (%)	**4.25**	**3.18**	**RSD (%)**	**3.79**	**1.20**
Toluene	Required Conc.(µg/L)		Ethylbenzene	Required Conc.(µg/L)	
	1.00	20.00		1.00	20.00
	Experimental Conc.			Experimental Conc.	
	0.97	20.97		0.83	18.18
	1.04	20.84		0.93	17.38
	1.02	21.01		0.88	19.03
	0.98	21.91		0.81	19.97
	1.15	21.31		1.12	20.77
MEAN	1.03	21.21	MEAN	0.91	19.07
STEVA	0.03	0.49	STDEVA	0.05	1.11
RSD (%)	**3.33**	**2.31**	**RSD (%)**	**5.59**	**5.84**
MP-Xylene	Required Conc.(µg/L)		O-Xylene	Required Conc.(µg/L)	
	1.00	20.00		1.00	20.00
	Experimental Conc.			Experimental Conc.	
	1.01	18.46		1.26	21.42
	1.06	17.59		1.18	20.66
	1.01	18.89		1.08	21.52
	0.96	19.48		0.99	22.56
	0.81	20.94		0.80	20.52
MEAN	0.97	19.07	MEAN	1.06	21.33
STEVA	0.04	0.80	STDEVA	0.11	0.78
RSD (%)	**4.38**	**4.17**	**RSD (%)**	**10.84**	**3.65**

Table 3.18. RSD(%) Values for Concentration Values 1 and 20µg/L.

As expected the RSD% values for the 1µg/L standard are higher than those calculated for the 20µg/L standard. Note that The RSD's for MTBE, benzene, toluene, ethylbenzene and m-p-xylene are similar, whilst the RSD for o-xylene is much higher.

Linearity of Calibration Curve.

The linearity of the calibration curve is an important measure of the quality of an analytical method. Linearity can be expressed by the r^2 value of a calibration curve. Linearity was established to over 1 order of magnitude using calibration standards 1, 10, 15 and 20µg/L. Figures 3.17 to 3.22 present GC-MS calibration curves for two calibration sets within the same GC-MS run, for MTBE and BTEX compounds.

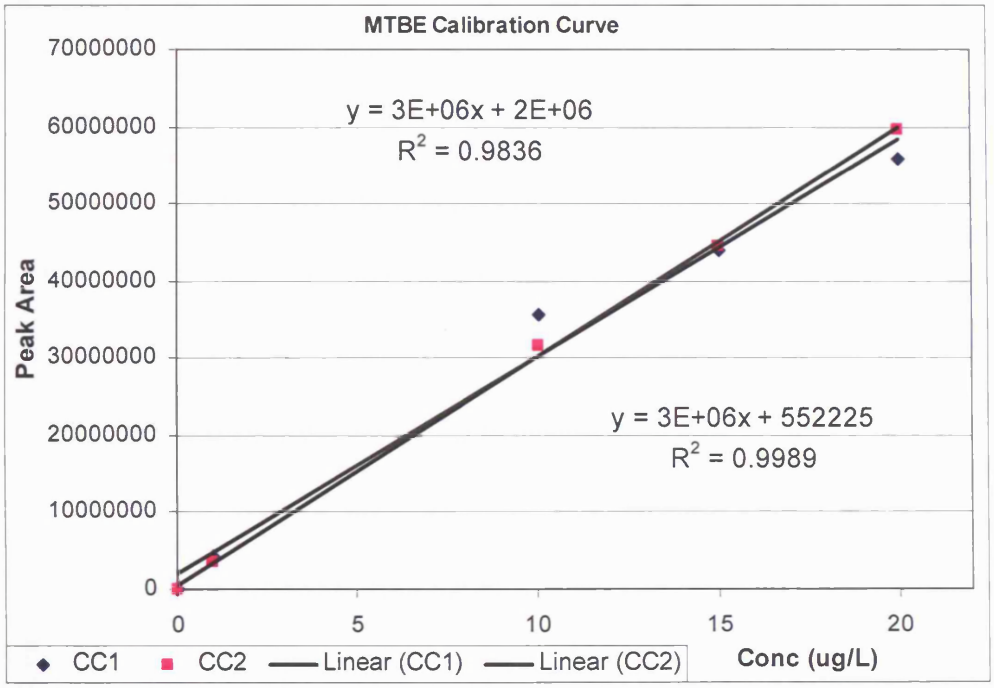


Figure 3.17. Linearity Curve for MTBE.

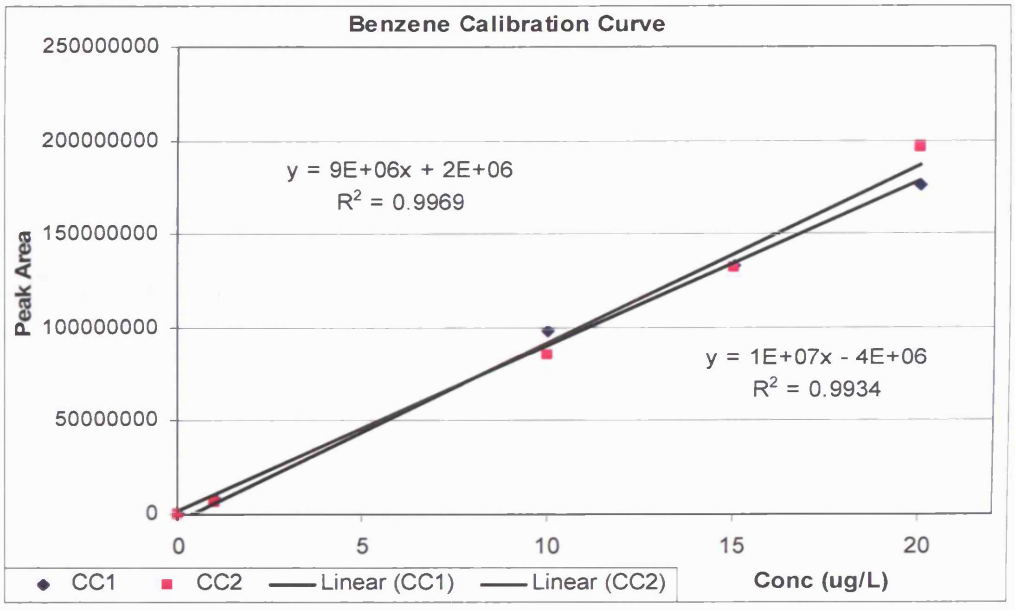


Figure 3.18. Linearity Curve for Benzene.

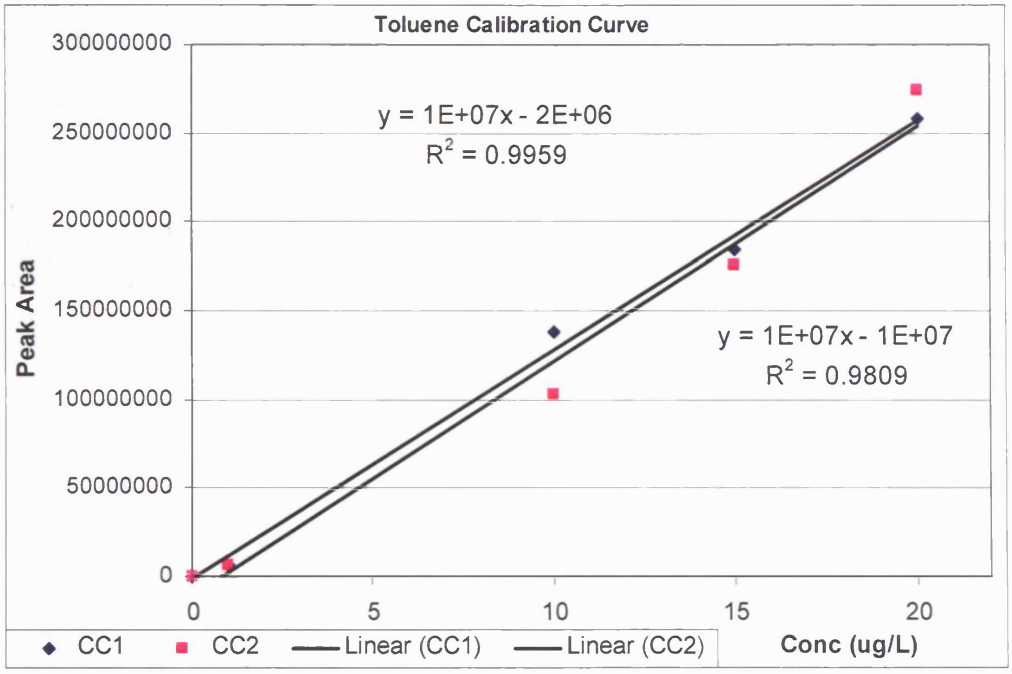


Figure 3.19. Linearity Curve for Toluene.

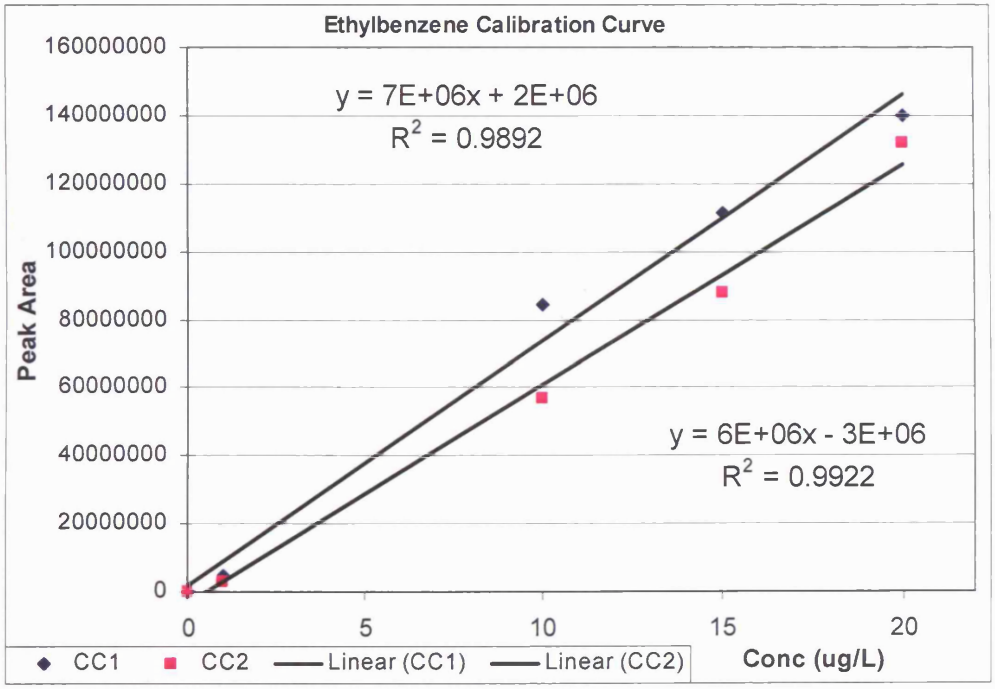


Figure 3.20. Linearity Curve for Ethylbenzene.

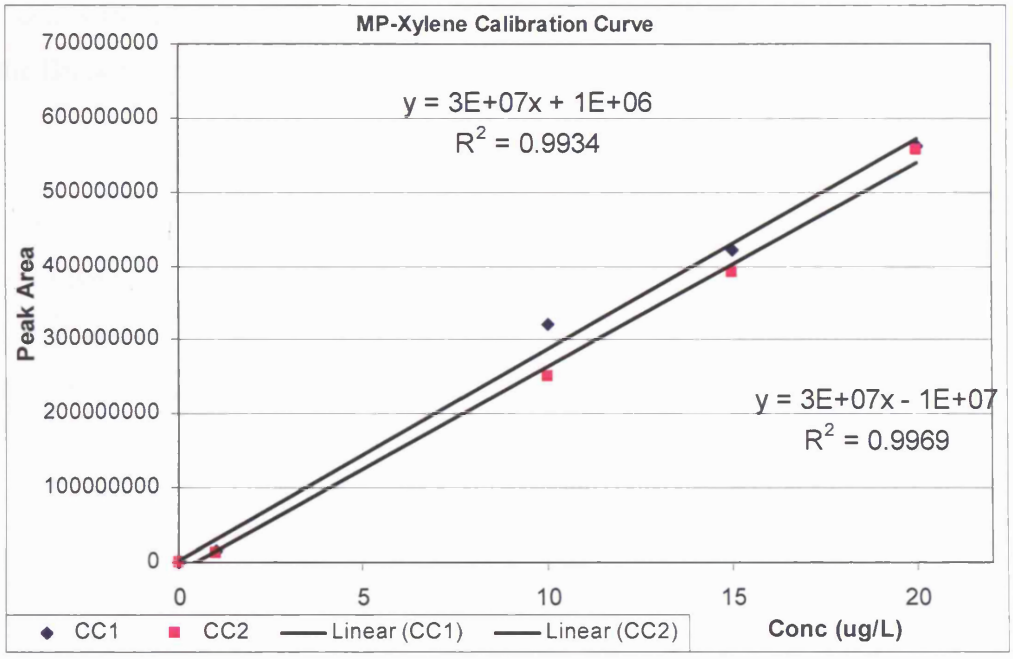


Figure 3.21. Linearity Curve for MP-Xylene.

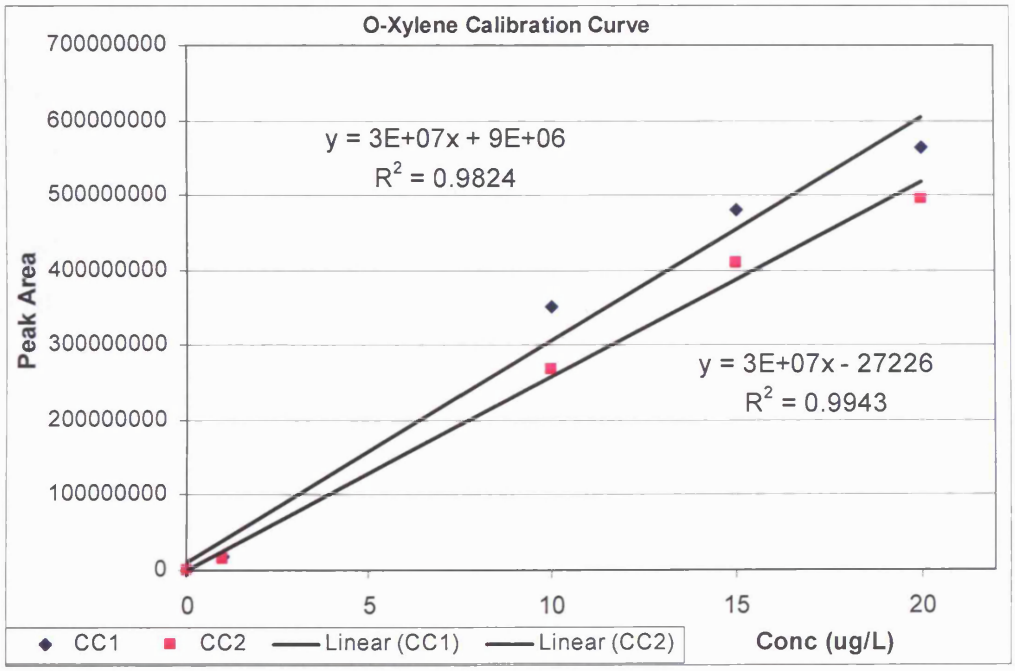


Figure 3.22. Linearity Curve for O-Xylene.

Method Comparison.

The method developed throughout the experimental phase of the project was compared to the method proposed by Bianchi *et al* (2002). Comparisons are also made between the USEPA method 524.2.

Table 3.19 details the LOD for the method developed for the fuel oil project, and the Bianchi method.

	New Method (µg/L)	USEPA Method 524.2 (µg/L)	Bianchi Method (ng/L)
MTBE	0.73	-	3.3
Benzene	0.71	0.019	6.0
Toluene	1.12	0.015	12.9
Ethylbenzene	1.24	0.006	22.6
m-p-Xylene	1.90	0.011	5.9
o-Xylene	1.44	0.009	2.8

Table 3.19. Comparison of LOD for New Method and Bianchi Method.

Referring to table 3.19 it can be seen that USEPA method and the Bianchi method both achieved lower LODs than the new GC method. In the case of the Bianchi method, the LODs achieved were substantially lower. However, it can be noted that the aim of the new method was not to achieve comparable LODs, but instead to develop a rapid/ automated GC-MS procedure.

Table 3.20 details r^2 values for typical calibration curves throughout the new method and the Bianchi method.

	New Method r^2	Bianchi Method r^2
MTBE	0.99	0.81
Benzene	0.99	0.94
Toluene	0.98	0.87
Ethylbenzene	0.99	0.91
m-p-Xylene	0.99	0.98
o-Xylene	0.99	0.98

Table 3.20. Comparison of r^2 Values for New Method and Bianchi Method.

Referring to table 3.20 it can be seen that the new method achieved better r^2 values than the Bianchi method.

In conclusion of the GC-MS method developed and implemented throughout this study; the method exceeded the requirements for the rapid automated determination of MTBE and benzene throughout the project using P&T. However, the quantification of TEX compounds proved more difficult due to the problems associated with inferior compound separation, and interference from DBPs.

The new method was compared to other accepted GC-MS methods, where the LODs obtained were found to be lower in both the Bianchi method and USEPA Method 524.2. However, this did not take into account the fact that the new method developed did not require such low LODs, and differed to the other methods in its speed and automation.

3.4. Problems Encountered during Experimental Phase.

RSSCT

Design Modifications.

The RSSCT pre-test highlighted a number of problems with respect to the use of the RSSCT in the removal of fuels oil compounds from synthetic feed water. Three problems were found to affect the capacity for the RSSCT to provide reproducible, reliable results;

1) Loss of the fuel oil compounds from the influent tanks through volatilisation.
2) The growth of microorganisms on the tank walls.
3) Increase in head loss leading to blockage of the carbon bed.

It is possible that the increase in head loss was due to fouling within the carbon column. This could have been caused by the precipitation of carbonates or the growth of microorganisms (a term called fouling). A number of modifications were made to the RSSCT in an attempt to resolve the problem. In order to reduce volatilisation, one of the influent tanks was fitted with a cooler. A timer was used on the cooler to maintain the temperature at approximately 12°C. The two influent tanks were fitted with a re-circulating pump to maintain a uniform temperature. The lower temperature was also intended to reduce bacterial growth. Floating lids were manufactured in an effort to reduce the loss of volatile hydrocarbons. The lids were PTFE coated and were designed to drop as the water

levels within the influent tanks fell. However, due to the tapered influent tanks, the lids could not cover the entire surface of the water.

The compaction of the carbon bed led to an increase in head loss through the column. Eventually this caused the failure of the peristaltic pump and the flow through the column stopped. As the carbon was removed from the column after the pre-test the PAC was found to have formed a plug. Under examination, the pores within the sintered discs had become blocked with PAC and were replaced. The steel columns were replaced with purpose-designed glass columns to study the behaviour of the carbon bed in normal and backwash flow direction.

CHAPTER 4: RESULTS.

Chapter 4 presents the results of the experimental phase of the present study. The experimental phase of the project was designed to investigate elements of the simultaneous removal of MTBE and BTEX from contaminated groundwater. The remedial process investigated throughout the present study utilises air-stripping and adsorption in series, where stringent global remediation targets for drinking water are adhered to.

Average removal efficiency (ARE%), capacity and breakthrough data is presented throughout Chapter 4 and compared with previous studies in Chapter 5. Where possible optimum parameters are also presented throughout Chapter 4.

The choice of remediation methods, contaminant influent levels, experimental variables and the implementation of the Taguchi method are clearly presented in Section 1.8 of Chapter 1 and Section 3.3 of Chapter 3. The experimental aims are presented in Chapter 2.

Firstly, the air-stripping results are presented in tabulated and graphical form. The results are interpreted throughout the text and are then summarised.

Secondly the adsorption column tests are presented in tabulated and graphical form. The results are also interpreted throughout the text and where possible, comparisons are made between tests. The results are then summarised.

Finally, the joint experimental are expressed with respect to the Taguchi orthogonal array.

Experimental trials are identified throughout the results chapter by the experimental numbers assigned to the runs in Table 3.13 (Section 3.2.8 of Chapter 3).

Chapter 4 includes data for MTBE and benzene compounds only. Toluene, ethylbenzene and xylene (TEX) compounds proved to be difficult to both identify and quantify on the GC-MS. The reasons of which are presented in Section 3.3.3 – 3.3.4 of Chapter 3. An example set of TEX results are presented in Appendix D.

Note that selective degradation of benzene occurred throughout Runs 7 and 8. It was assumed that this was caused by the excessive sample storage period experienced throughout the tests (caused by a GC-MS fault). Therefore results for MTBE are only available for Runs 7 and 8.

No relevant data was collected from the RSSCT experiments, this was due to the unsuitability of the apparatus in for testing fuel oils. The problems with the RSSCT are detailed section 3.4 of Chapter 3. RSSCT pre-test experimental data is detailed in Appendix B. Pilot-Plant pre-test results are presented in Appendix E.

4.1. Experimental Error.

4.1.1. Expression of Significant Figures throughout Results Chapter.

On the basis of the limited statistical analysis performed on the GC-MS method (Section 3.3.4 of Chapter 3), throughout Chapter 4 concentration values <10μg/L were expressed to 2 significant figures (one decimal place) and concentration values >10μg/L were expressed to 2 significant figures (zero decimal places). These significant figures were deemed to be acceptable within the remit of the study.

4.1.2. Estimation of Experimental Error.

Estimation of the experimental error was based upon;

1) RSD% for benzene and MTBE (Section 3.3.4 of Chapter 3)
2) Repeat samples taken from the pilot plant.

Referring to the first estimate, the RSD% took into account the error of the GC-MS method. The second estimate refers to the intra-test pilot-plant procedure (sampling errors, operator errors etc).

Referring to Section 3.3.4 of Chapter 3, the RSD% for benzene at 1μg/L was 3.79% and the RSD% for MTBE at 1μg/L was 4.25%. An RSD% of 4.0% was therefore assumed for benzene and MTBE.

The intra-test procedure error was calculated by comparing repeat samples taken from the pilot-plant. The number of repeat samples that could actually be run on the GC-MS was small. For the purpose of the intra-test procedure errors, repeat samples from Run 2 were compared. These are presented in Table 4.1.

	+/- Percentage
MTBE	6.6
Benzene	2.4

Table 4.1. Intra-Test Error Associated with Pilot-Plant.

From the results detailed in Table 4.1, an overall pilot-plant procedure error of 6% was assumed.

Overall, an estimated error of 10% was assumed for the pilot-plant results. These are expressed graphically as error bars. However, it is important to note that this is an estimated error only.

4.2. Air-Stripping Results.

Tables 4.2 – 4.6 present the air-stripping results for runs 1-8 and the Run 8 Repeat test (the Taguchi verification test). The tables are designed to present the data from each test, not to provide a means for interpretation. However, average removal efficiencies (ARE%) are included within the tables to provide an initial indication of the performance of each process.

Note that the Taguchi experimental method required that a verification test be run in order to verify the results of the statistical analysis. Chapter 4.4 refers to the fact that the optimum process variables were identical to the variables used in Run 8.

All figures within the tables are presented as concentrations (μg/L). Values expressed throughout Chapter 4 as <1 μg/L represent those below the LOD of the GC-MS apparatus.

ARE% calculations throughout Chapter 4 were performed in the following manner;

$$100\text{-}((\frac{Y}{X})\times 100) \qquad \textbf{(eqn. 4.1)}$$

Where X = Influent concentration (μg/L) and Y = Effluent concentration (μg/L). Calculations were made for each time samples were taken on the pilot-plant and the average taken from the entire set of data.

Table 4.2 presents the air-stripping results from Run 1 – 2. NDA = no data available.

RUN 1		Influent (ug/L)	Effluent (ug/L)	RUN 2		Influent (ug/L)	Effluent (ug/L)
Day 1	MTBE	69	108	Day 1	MTBE	24	22
	BENZENE	51	12		BENZENE	54	21
Day 4	MTBE	145	71	Day 4	MTBE	20	12
	BENZENE	94	7.4		BENZENE	65	12
Day 6	MTBE	233	83	Day 6	MTBE	15	13
	BENZENE	177	11		BENZENE	42	13
Day 8	MTBE	103	47	Day 8	MTBE	35	25
	BENZENE	70	7.3		BENZENE	92	18
Day 12	MTBE	198	59	Day 11	MTBE	16	14
	BENZENE	177	7.2		BENZENE	57	10
Day 14	MTBE	199	139	Day 13	MTBE	23	14
	BENZENE	162	20		BENZENE	85	12
Day 16	MTBE	NDA	128	Day 15	MTBE	22	21
	BENZENE	NDA	19		BENZENE	43	13
Day 19	MTBE	193	96	Day 19	MTBE	28	20
	BENZENE	199	13		BENZENE	141	29
Day 21	MTBE	219	110	Day 21	MTBE	21	18
	BENZENE	152	15		BENZENE	96	23
				Day 25	MTBE	25	21
					BENZENE	70	13
				Day 26	MTBE	27	21
					BENZENE	68	14
MTBE	Average	175	84	MTBE	Average	23	18
	ARE%		41		ARE%		20
Benzene	Average	135	12	Benzene	Average	74	16
	ARE%		90		ARE%		81

Table 4.2. Run 1 and 2 Air-Stripping Results.

Table 4.3 presents the air-stripping results from Run 3 – 4. NDA = no data available.

RUN 3		Influent (ug/L)	Effluent (ug/L)	RUN 4		Influent (ug/L)	Effluent (ug/L)
Day 1	MTBE	60	5.3	Day 1	MTBE	150	107
	BENZENE	36	10		BENZENE	102	23
Day 3	MTBE	42	6.9	Day 3	MTBE	114	78
	BENZENE	27	16		BENZENE	72	19
Day 6	MTBE	48	4.1	Day 6	MTBE	162	136
	BENZENE	22	10		BENZENE	66	17
Day 8	MTBE	112	9.5	Day 8	MTBE	182	137
	BENZENE	62	19		BENZENE	139	30
Day 11	MTBE	36	4.8	Day 13	MTBE	107	58
	BENZENE	16	5.6		BENZENE	80	18
Day 13	MTBE	22	4.5	Day 15	MTBE	210	158
	BENZENE	45	5.1		BENZENE	176	46
Day 15	MTBE	121	15	Day 17	MTBE	152	83
	BENZENE	36	4.3		BENZENE	115	18
Day 18	MTBE	54	5.1	Day 20	MTBE	181	55
	BENZENE	8.9	8.8		BENZENE	153	24
Day 20	MTBE	78	3.4	Day 21	MTBE	208	28
	BENZENE	10	8.0		BENZENE	34	14
Day 21	MTBE	84	5.1				
	BENZENE	13	11				
MTBE	Average	67	6.4	MTBE	Average	163	93
	ARE%		89		ARE%		41
Benzene	Average	28	10	Benzene	Average	164	23
	ARE%		52		ARE%		76

Table 4.3. Run 3 and 4 Air-Stripping Results.

Table 4.4 presents the air-stripping results from Run 5 – 6. NDA = no data available.

RUN 5		Influent (ug/L)	Effluent (ug/L)	RUN 6		Influent (ug/L)	Effluent (ug/L)
Day 2	MTBE	28	22	Day 1	MTBE	3.2	3.1
	BENZENE	36	9.3		BENZENE	34	7.6
Day 4	MTBE	72	26	Day 3	MTBE	19	5.7
	BENZENE	47	10		BENZENE	105	11
Day 6	MTBE	49	20	Day 6	MTBE	13	3.5
	BENZENE	27	8.0		BENZENE	65	5.6
Day 9	MTBE	50	18	Day 8	MTBE	13	3.5
	BENZENE	26	7.6		BENZENE	89	7.5
Day 11	MTBE	51	11	Day 10	MTBE	14	4.4
	BENZENE	23	5.7		BENZENE	85	7.0
Day 14	MTBE	82	12	Day 13	MTBE	4.3	3.6
	BENZENE	23	6.4		BENZENE	47	5.3
Day 16	MTBE	69	23	Day 15	MTBE	6.7	1.9
	BENZENE	51	7.4		BENZENE	43	2.1
Day 18	MTBE	40	21	Day 17	MTBE	18	2.1
	BENZENE	20	6.7		BENZENE	7.4	2.6
Day 21	MTBE	31	17	Day 20	MTBE	10	3.4
	BENZENE	19	5.8		BENZENE	4.3	1.1
				Day 21	MTBE	7.2	2.5
					BENZENE	26	1.4
MTBE	Average	53	19	MTBE	Average	11	3.4
	ARE%		59		ARE%		60
Benzene	Average	30	7.5	Benzene	Average	51	5.1
	ARE%		74		ARE%		85

Table 4.4. Run 5 and 6 Air-Stripping Results.

Table 4.5 presents the air-stripping results from Run 7 – 8. NDA = no data available.

RUN 7		Influent (ug/L)	Effluent (ug/L)	RUN 8		Influent (ug/L)	Effluent (ug/L)
Day 1	MTBE	8.7	8.1	Day 1	MTBE	15	4.0
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 2	MTBE	8.7	5.7	Day 3	MTBE	15	3.3
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 3	MTBE	3.6	3.0	Day 6	MTBE	6.4	2.9
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 7	MTBE	7.9	4.4	Day 8	MTBE	4.4	2.4
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 9	MTBE	12	8.2	Day 10	MTBE	3.1	2.5
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 11	MTBE	2.6	2.2	Day 13	MTBE	18	5.4
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 14	MTBE	2.5	2.3	Day 15	MTBE	15	4.6
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 16	MTBE	2.3	2.0	Day 17	MTBE	14	5.5
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 18	MTBE	3.6	2.3	Day 20	MTBE	25	9.9
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
Day 21	MTBE	7.7	5.5	Day 21	MTBE	13	5.4
	BENZENE	NDA	NDA		BENZENE	NDA	NDA
MTBE	Average	6	4.4	MTBE	Average	13	4.6
	ARE%		24		ARE%		60
Benzene	Average	NDA	NDA	Benzene	Average	NDA	NDA
	ARE%		NDA		ARE%		NDA

Table 4.5. Run 7 and 8 Air-Stripping Results.

Table 4.6 presents the air-stripping results from Run 8 Repeat Test (Taguchi Verification Test). NDA = no data available.

RUN 8 REPEAT		Influent (ug/L)	Effluent (ug/L)
Day 1	MTBE	5.2	2.2
	BENZENE	61	5.3
Day 4	MTBE	6.3	2.1
	BENZENE	72	6.6
Day 6	MTBE	5.7	2.8
	BENZENE	101	12
Day 8	MTBE	9.7	8.6
	BENZENE	50	13
Day 11	MTBE	16	9.1
	BENZENE	127	17
Day 13	MTBE	8.8	6.0
	BENZENE	61	18
Day 15	MTBE	11	6.2
	BENZENE	119	22
Day 18	MTBE	11	6.3
	BENZENE	125	16
Day 20	MTBE	16	10
	BENZENE	106	10
Day 21	MTBE	11	10
	BENZENE	91	20
MTBE	Average	10	6.4
	ARE%		39
Benzene	Average	91	20
	ARE%		84

Table 4.6. Run 8 Repeat Test Air-Stripping Results.

The following section presents the air-stripping results in graphical form. Two types of graph are used to present the data;

- Influent and Effluent Concentration versus time.
- Influent Concentration and Air-Stripper Efficiency (2 No. Y-Axis) versus time.

The latter graph presents the removal efficiency of the air-stripper independently from the variable influent concentration. The air-stripping efficiency is then plotted against the influent concentration to examine the relationship between the influent concentration and the removal efficiency.

Run 1 MTBE.

Air-to-Water Ratio = 12

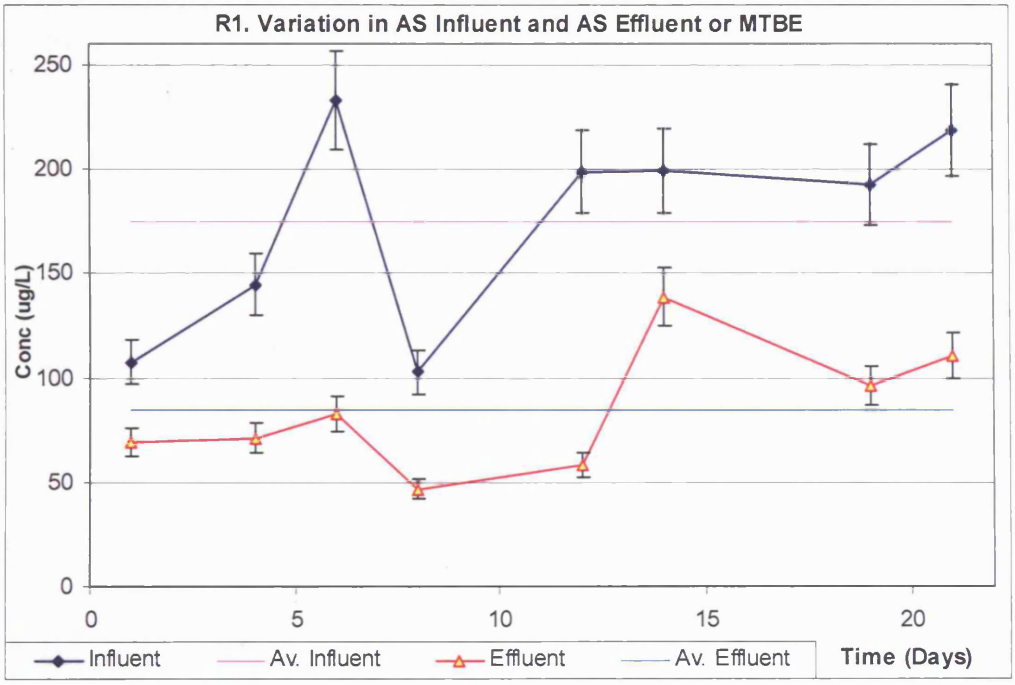


Figure 4.1. Graph to show Influent and Effluent Concentrations of MTBE during Run 1.

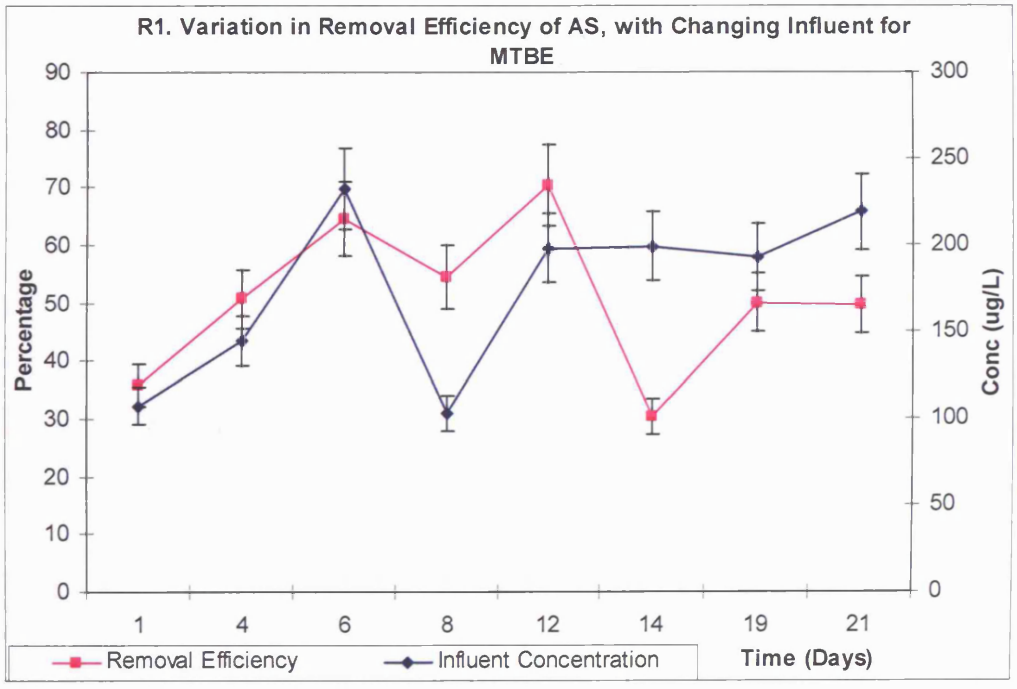


Figure 4.2. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 1.

Run 1 Benzene.

Air-to-Water Ratio = 12.

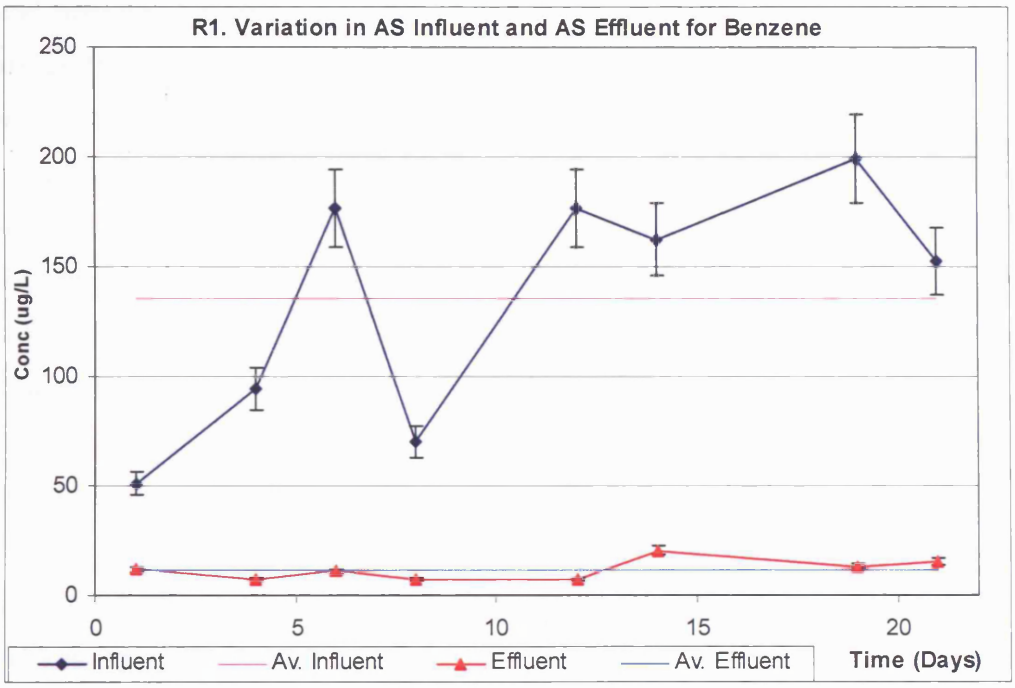


Figure 4.3. Graph to show Influent and Effluent Concentrations of Benzene during Run 1.

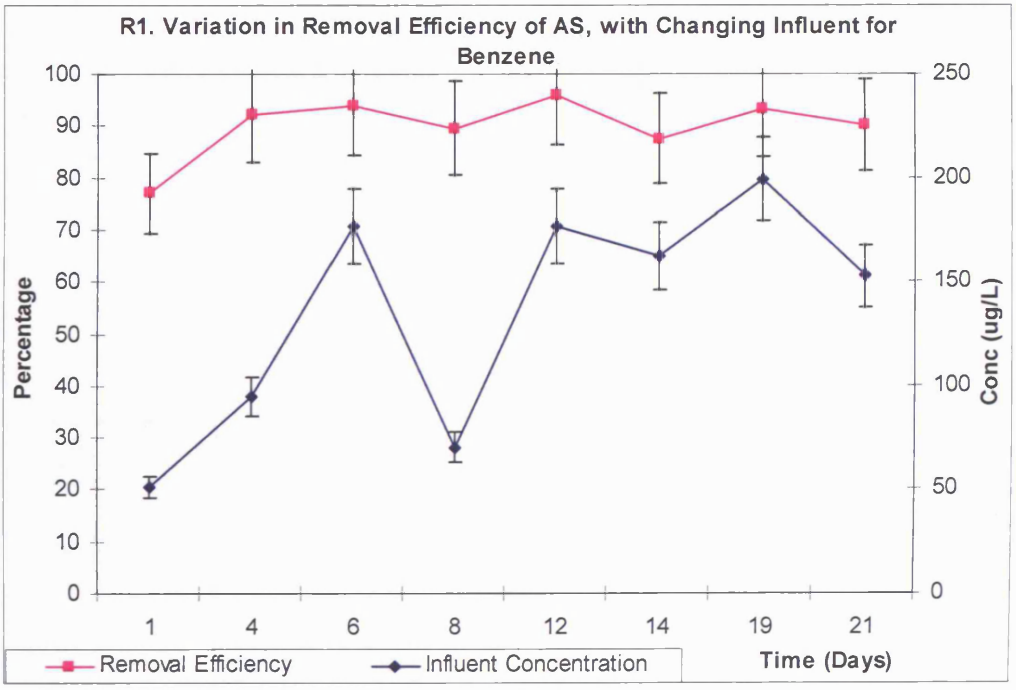


Figure 4.4. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 1.

Summary.

Influent concentrations experienced throughout Run 1 were high for both MTBE and benzene. Referring to Figure 4.1, as the influent concentration of MTBE varies, the concentration of MTBE in the effluent also varies. Referring to Figure 4.3, as the influent concentration of benzene varies, the effluent concentration remains relatively stable. This suggests that the removal efficiency of benzene is less affected by the variable influent concentration.

Referring to Figures 4.2 and 4.4 the removal efficiency for benzene was greater than that for MTBE. The removal efficiency of benzene was high even though a low air-to-water ratio was implemented. Generally, as the influent concentration for both MTBE and benzene increases, the removal efficiency of the air-stripper also increases.

Run 2 MTBE.

Air-to-Water Ratio = 12.

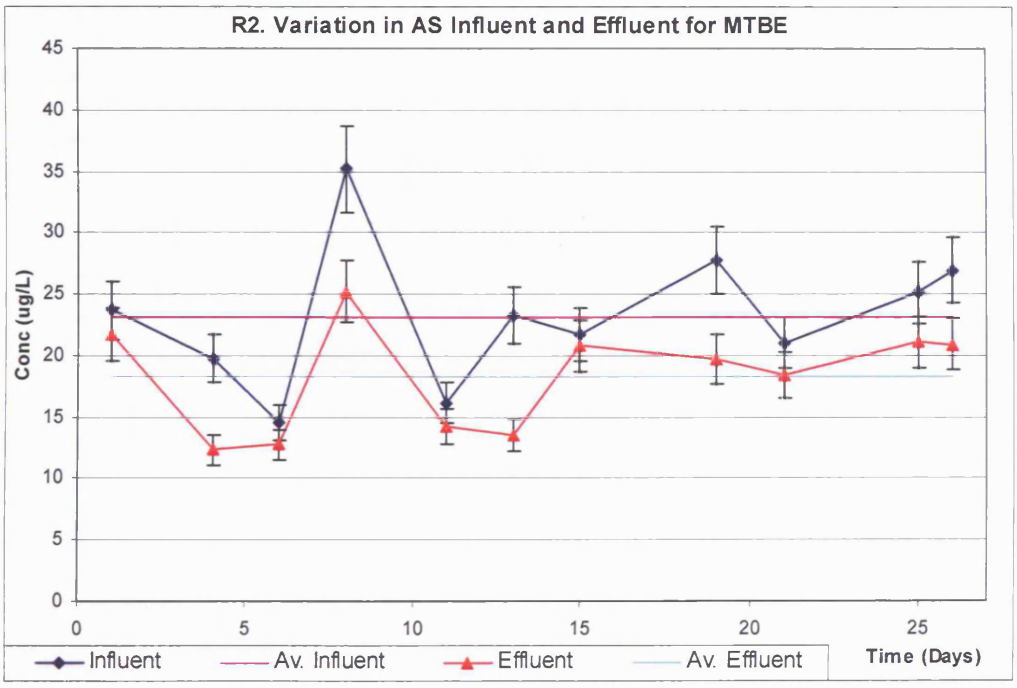


Figure 4.5. Graph to show Influent and Effluent Concentrations of MTBE, during Run 2.

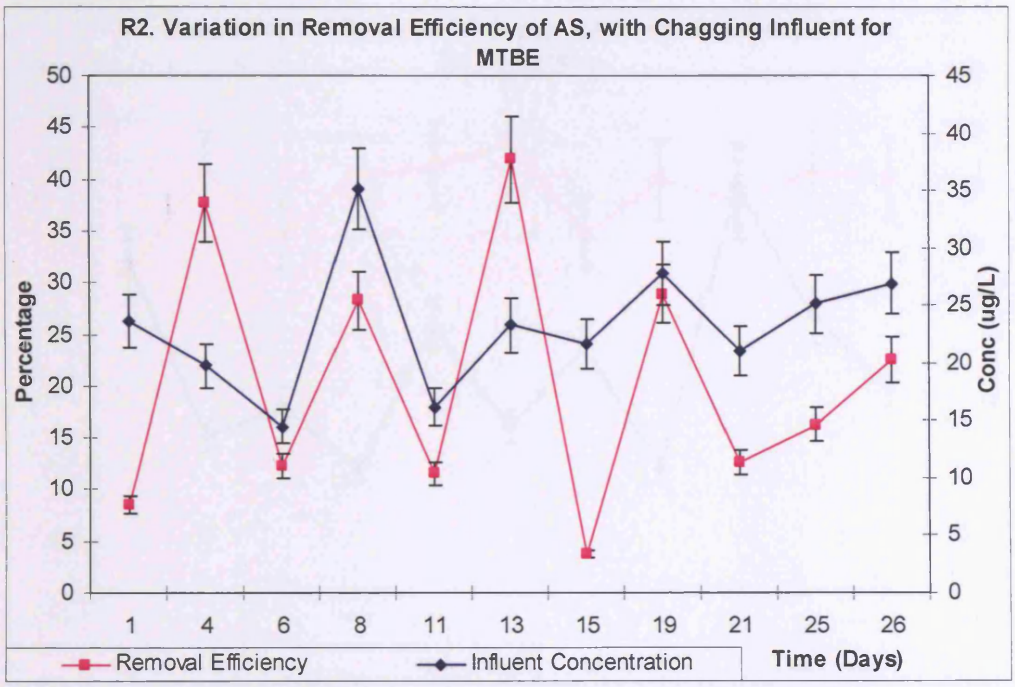


Figure 4.6. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 2.

Run 2 Benzene.

Air-to-Water Ratio = 12.

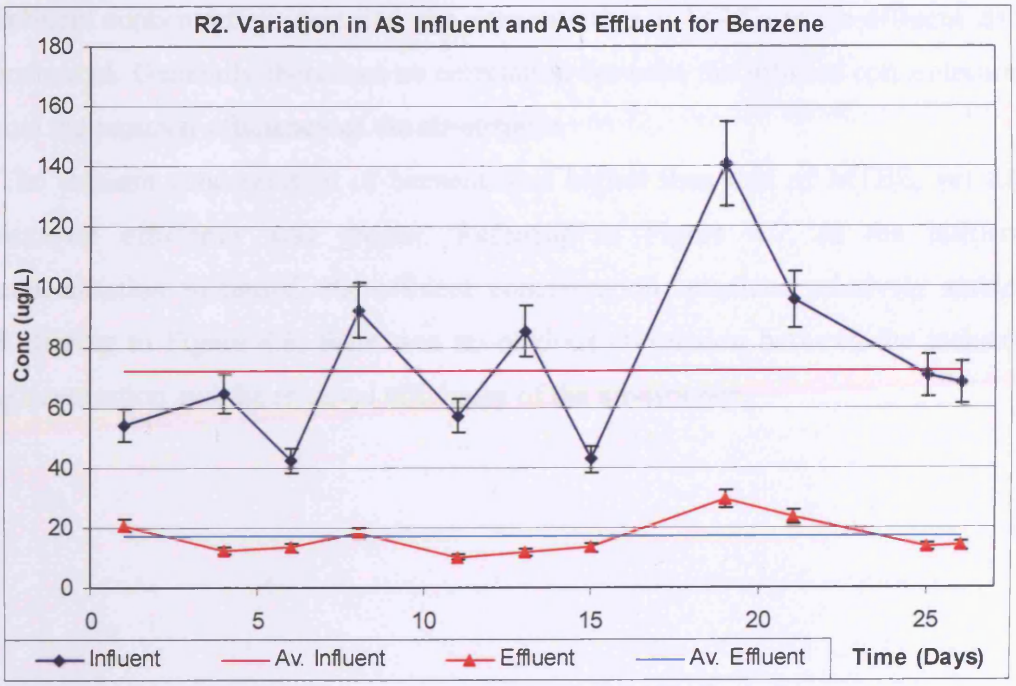


Figure 4.7. Graph to show Influent and Effluent Concentrations of Benzene, during Run 3.

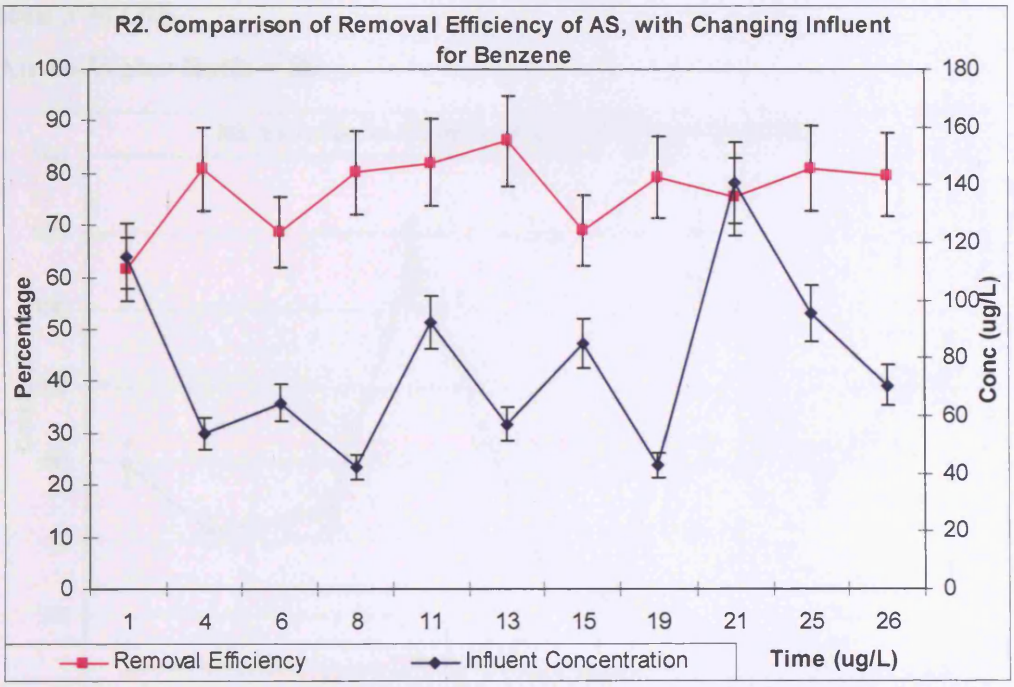


Figure 4.8. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 2.

Summary.

Referring to Figure 4.5 and 4.6, the removal efficiency of MTBE was low. As the influent concentration increased, the concentration of MTBE in the effluent also increased. Generally there was no correlation between the influent concentration and the removal efficiency of the air-stripper.

The influent concentration of benzene was higher than that of MTBE, yet the removal efficiency was greater. Referring to Figure 4.7, as the influent concentration increased, the effluent concentration remained relatively stable. Referring to Figure 4.8, there was no obvious correlation between the influent concentration and the removal efficiency of the air-stripper.

Run 3 MTBE.

Air-to-Water Ratio = 86.

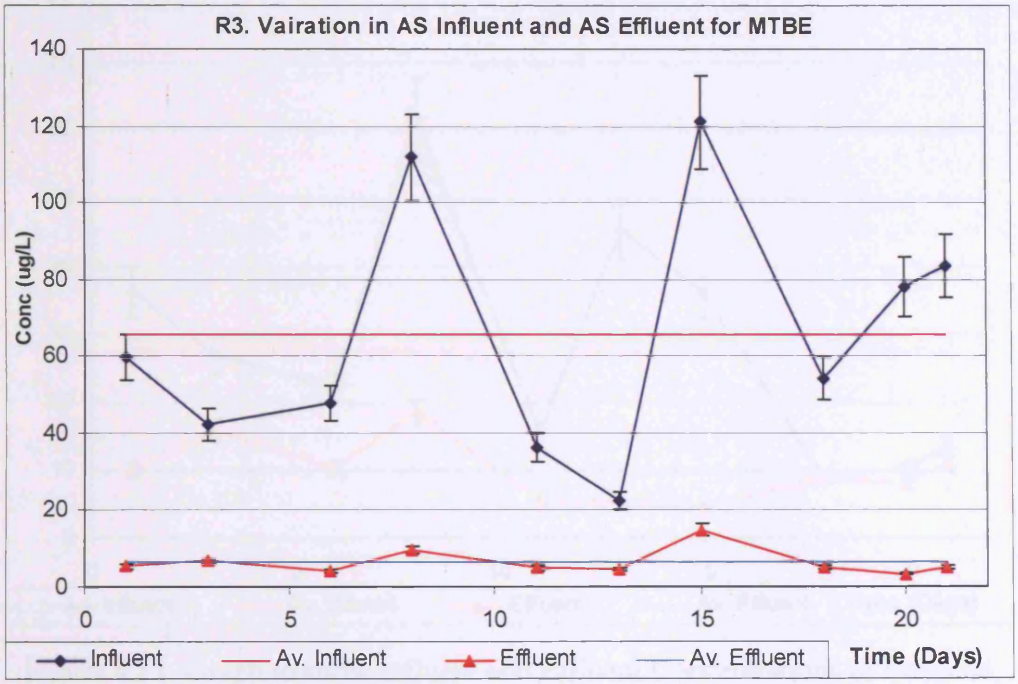


Figure 4.9. Graph to show Influent and Effluent Concentrations of MTBE, during Run 3.

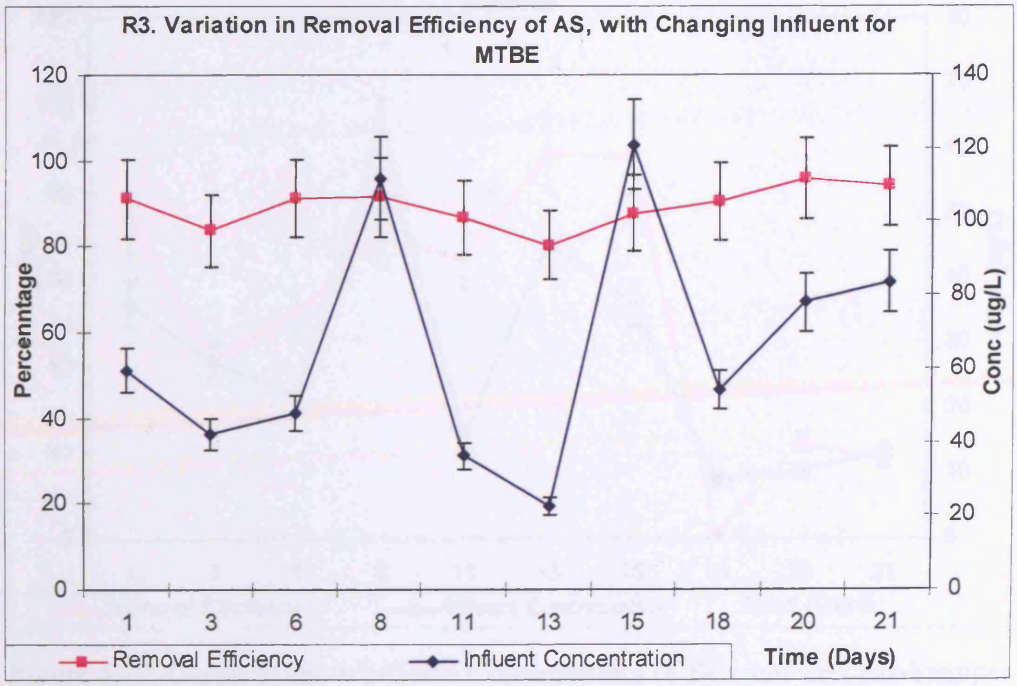


Figure 4.10. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 3.

Run 3 Benzene.

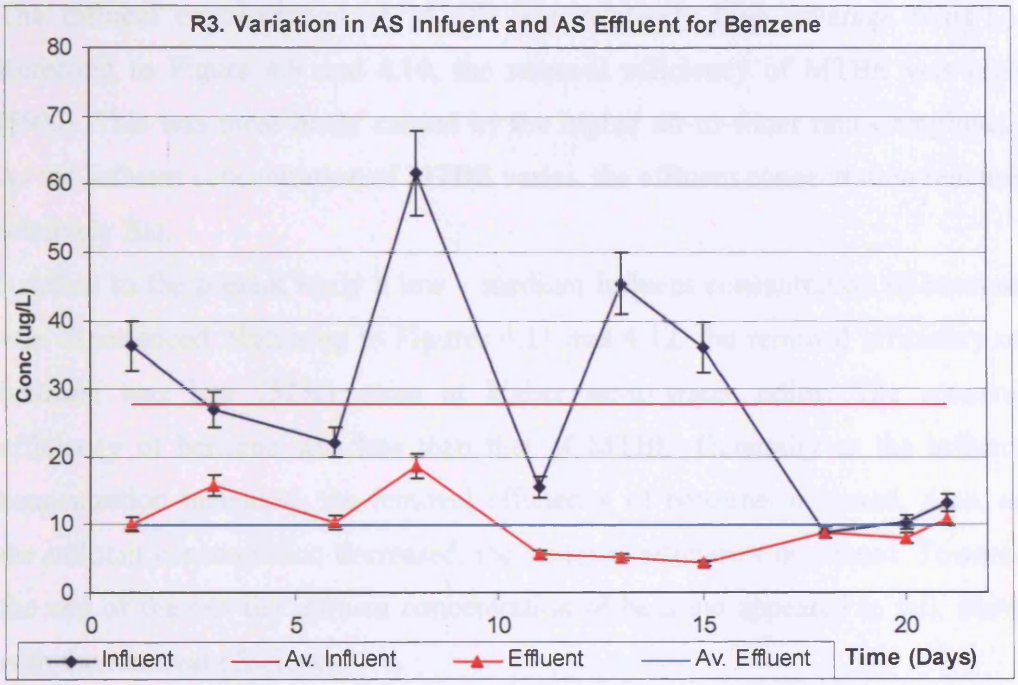


Figure 4.11. Graph to show Influent and Effluent Concentrations of Benzene, during Run 3.

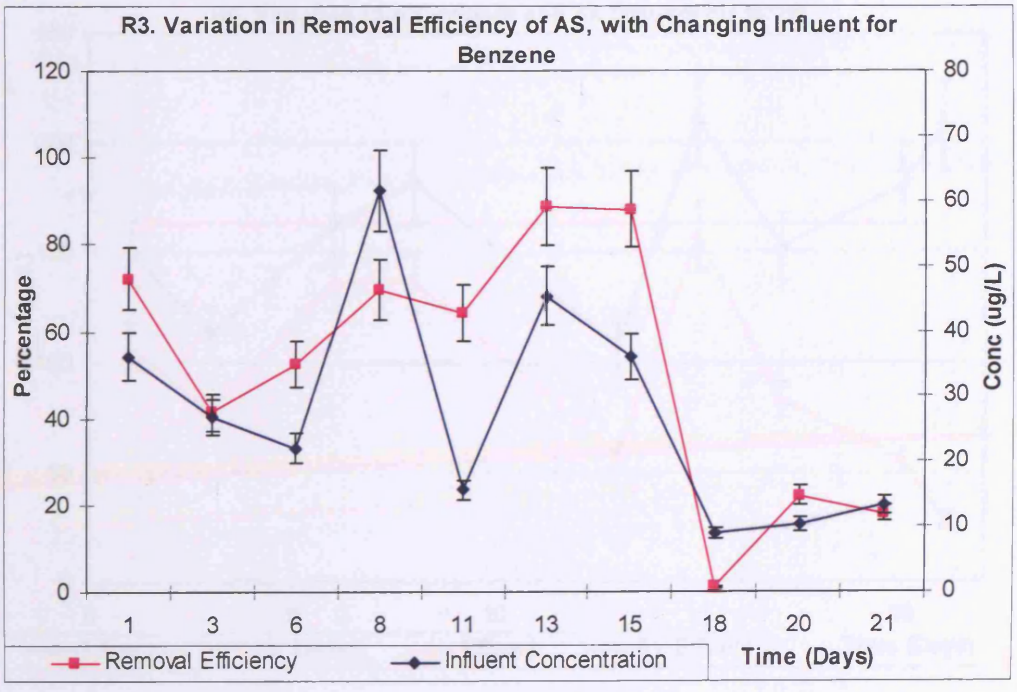


Figure 4.12. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 3.

Summary.

The influent concentration of MTBE was relatively high (average 67µg/L). Referring to Figure 4.9 and 4.10, the removal efficiency of MTBE was high (89%). This was most likely caused by the higher air-to-water ratios employed. As the influent concentration of MTBE varies, the effluent concentration remains relatively flat.

Relative to the present study a low – medium influent concentration of benzene was experienced. Referring to Figures 4.11 and 4.12, the removal efficiency of benzene was low (52%), even at higher air-to-water ratios. The removal efficiency of benzene was less than that of MTBE. Generally as the influent concentration increased, the removal efficiency of benzene increased. Also, as the influent concentration decreased, the removal efficiency decreased. Towards the end of the test the influent concentration of benzene appeared to fall, along with the removal efficiency.

Run 4 MTBE.

Air-to-Water Ratio = 9.

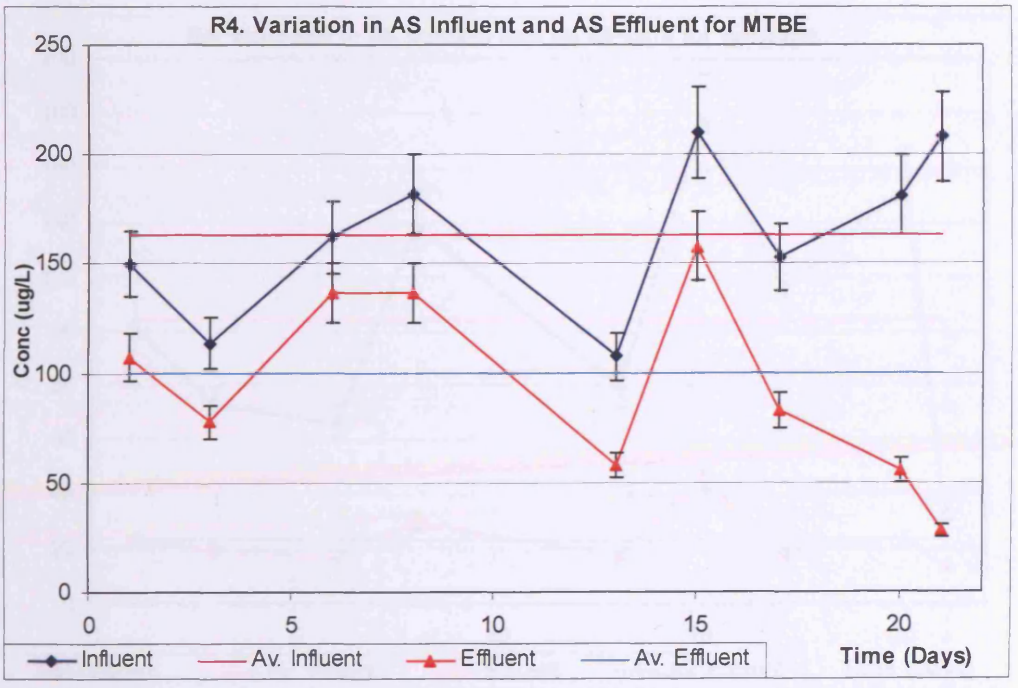


Figure 4.13. Graph to show Influent and Effluent Concentrations of MTBE, during Run 4.

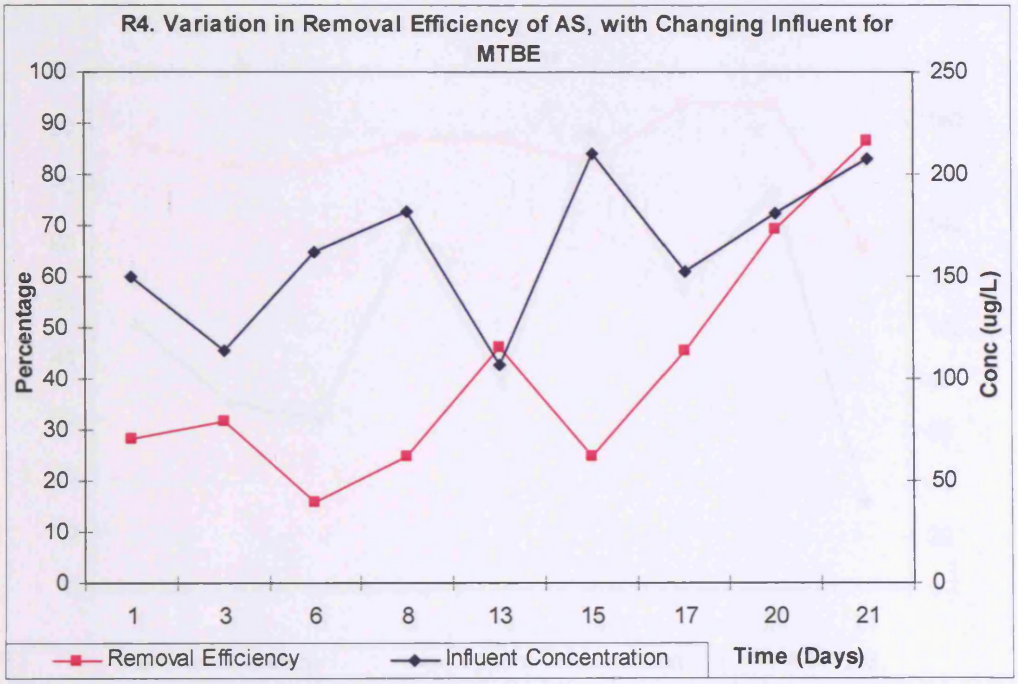


Figure 4.14. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 4.

Run 4 Benzene.

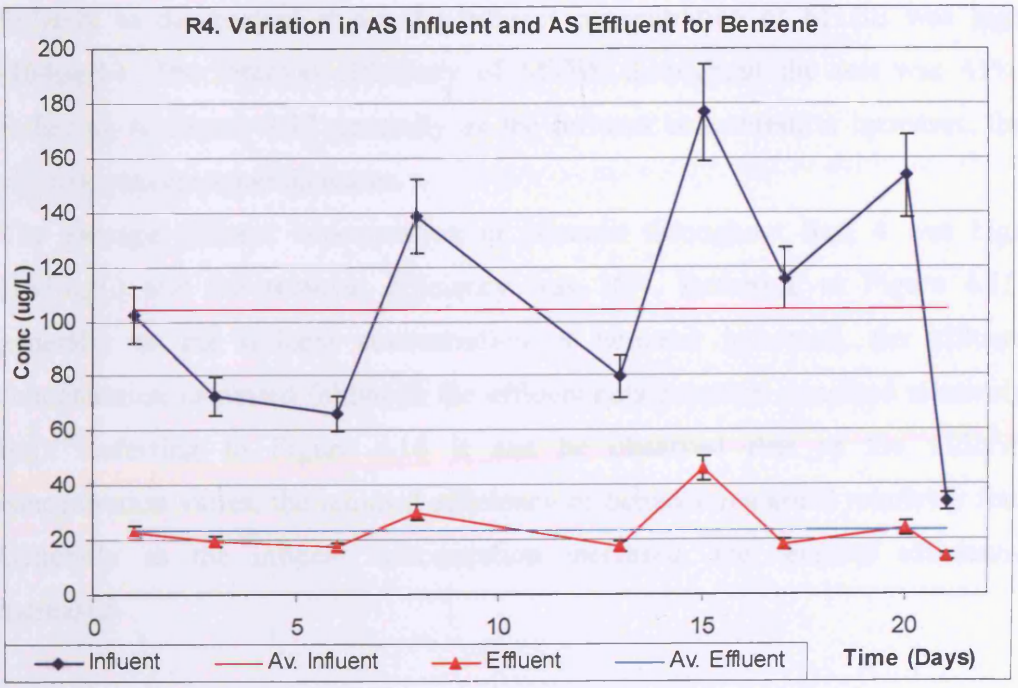


Figure 4.15. Graph to show Influent and Effluent Concentrations of Benzene, during Run 4.

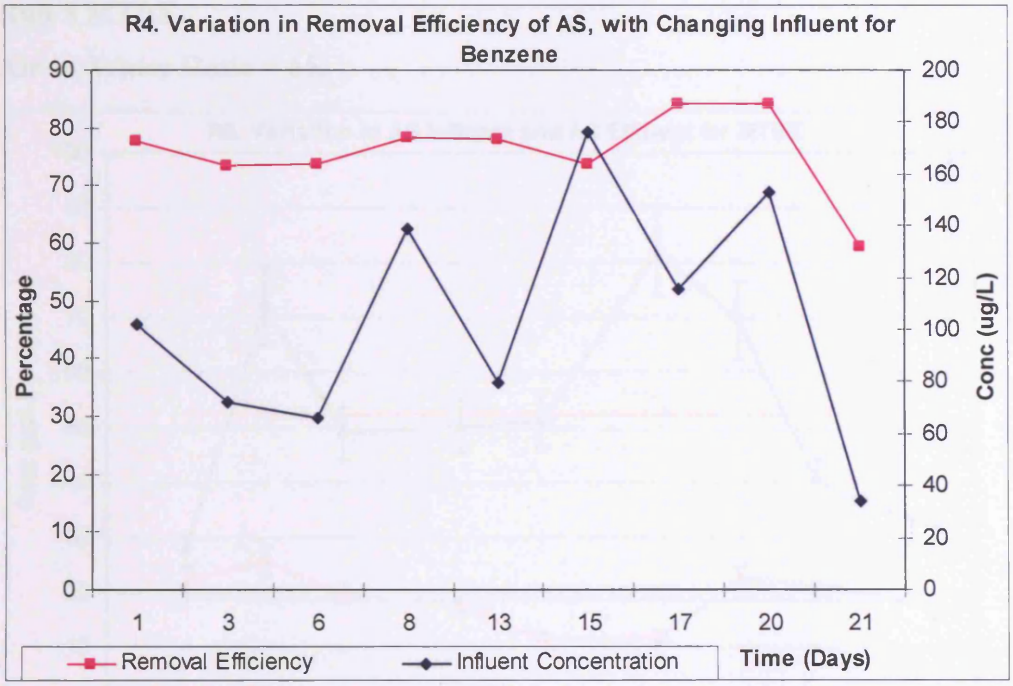


Figure 4.16. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 4.

Summary.

Relative to the present study, the influent concentration of MTBE was high (164µg/L). The removal efficiency of MTBE throughout the test was 41%. Referring to Figure 4.13 generally as the influent concentration increases, the effluent concentration increases.

The average influent concentration of benzene throughout Run 4 was high (163µg/L) and the removal efficiency was 76%. Referring to Figure 4.15, generally as the influent concentration of benzene increased, the effluent concentration increased (although the effluent concentration remained relatively flat). Referring to Figure 4.16 it can be observed that as the influent concentration varies, the removal efficiency of benzene remained relatively flat. Generally as the influent concentration increased, the removal efficiency increased.

Run 5 MTBE.

Air-to-Water Ratio = 65.

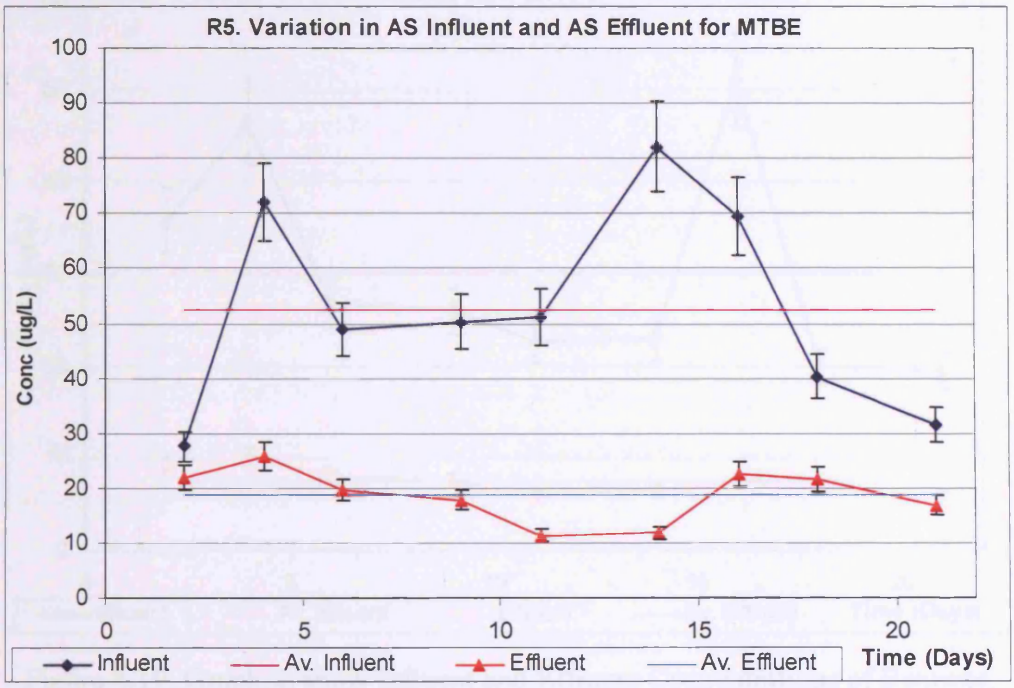


Figure 4.17. Graph to show Influent and Effluent Concentrations of MTBE, during Run 4.

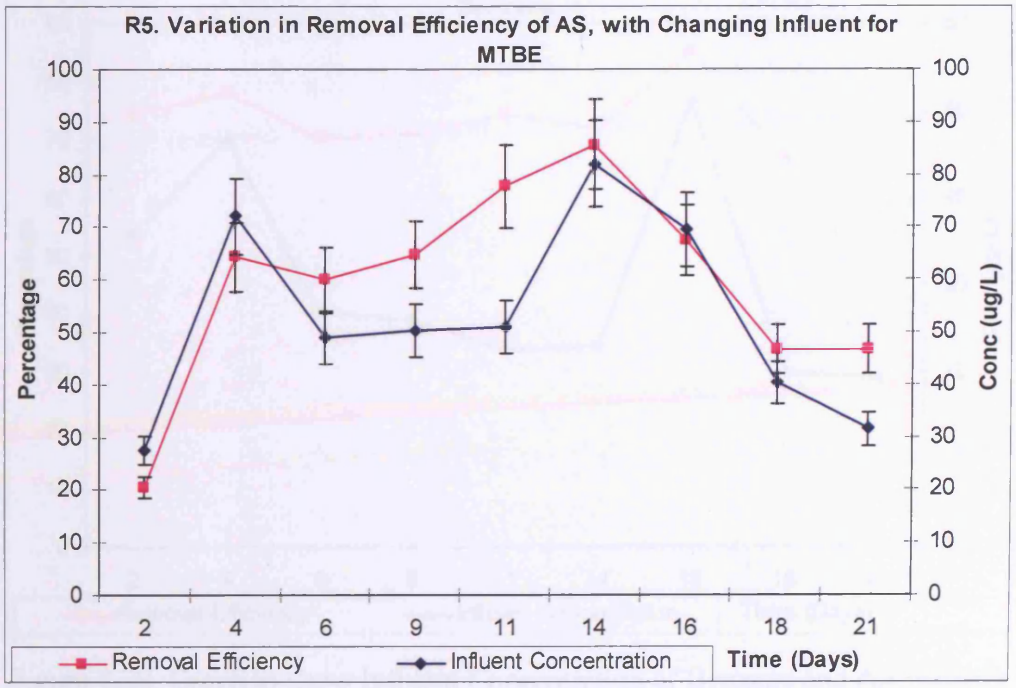


Figure 4.18. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 5.

Run 5 Benzene.

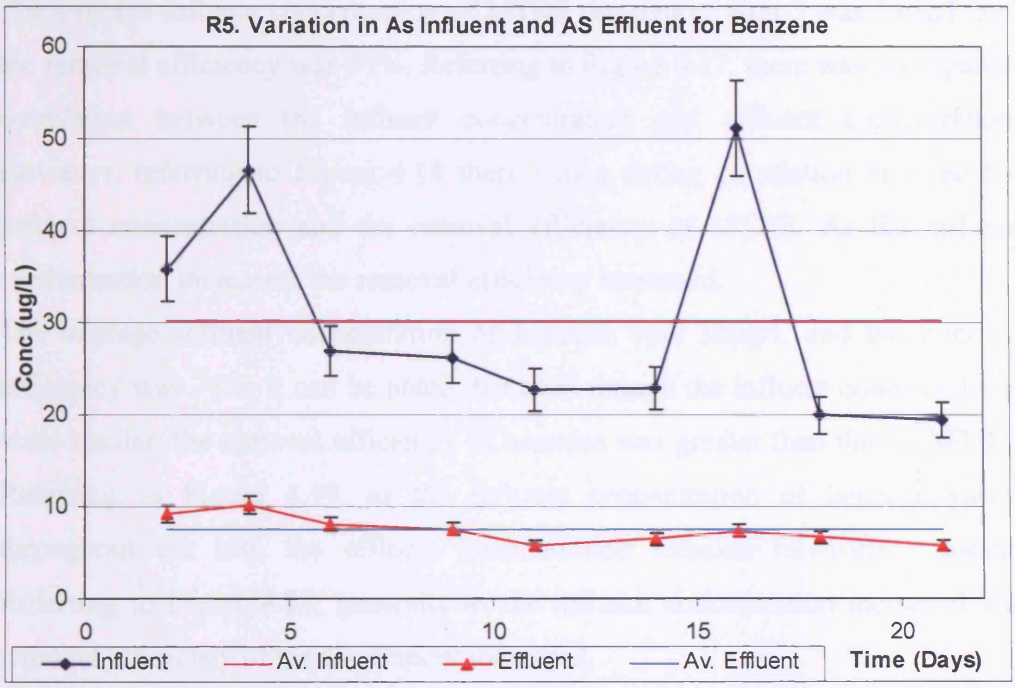


Figure 4.19. Graph to show Influent and Effluent Concentrations of Benzene, during Run 5.

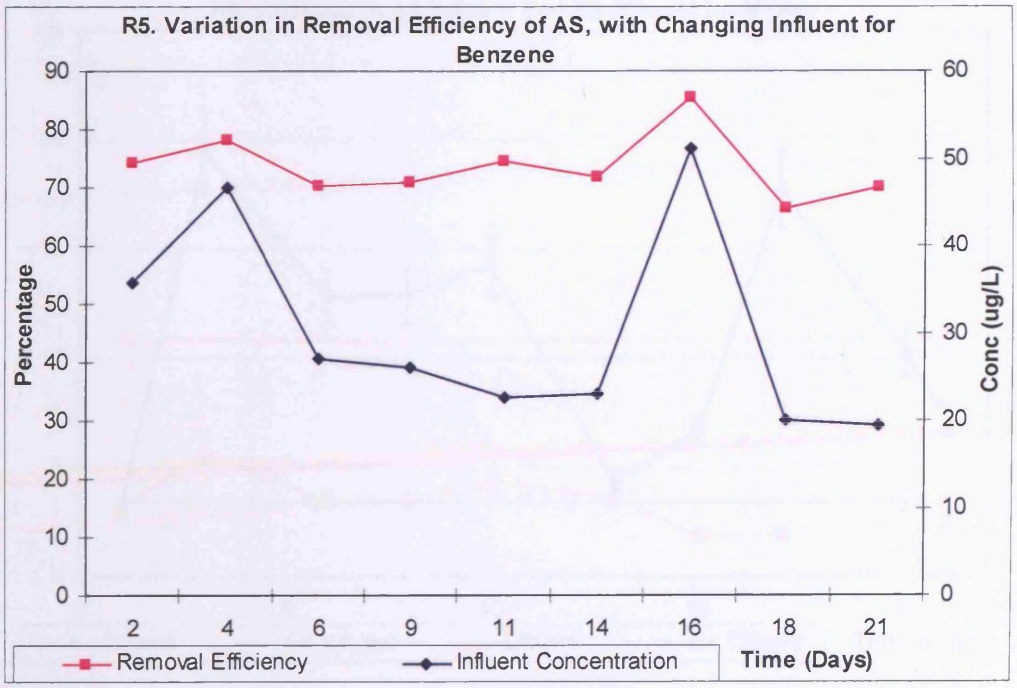


Figure 4.20. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 5.

Summary.

The average influent concentration of MTBE throughout Run 5 was 54µg/L and the removal efficiency was 59%. Referring to Figure 4.17, there was no apparent correlation between the influent concentration and effluent concentration. However, referring to Figure 4.18 there was a strong correlation between the influent concentration and the removal efficiency of MTBE. As the influent concentration increased, the removal efficiency increased.

The average influent concentration of benzene was 30µg/L and the removal efficiency was 74%. It can be noted that even though the influent concentrations were similar, the removal efficiency of benzene was greater than that of MTBE. Referring to Figure 4.19, as the influent concentration of benzene varies throughout the test, the effluent concentration remains relatively constant. Referring to Figure 4.20, generally as the influent concentration increased, the removal efficiency of the air-stripper increased.

Run 6 MTBE.

Air-to-Water Ratio 65.

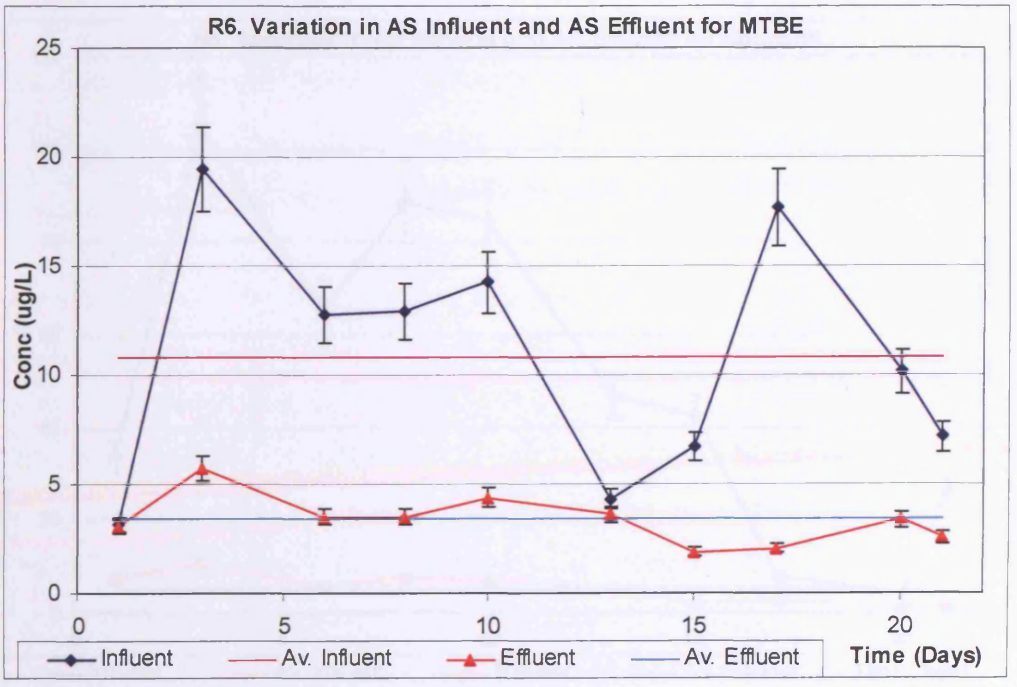


Figure 4.21. Graph to show Influent and Effluent Concentrations of MTBE, during Run 6.

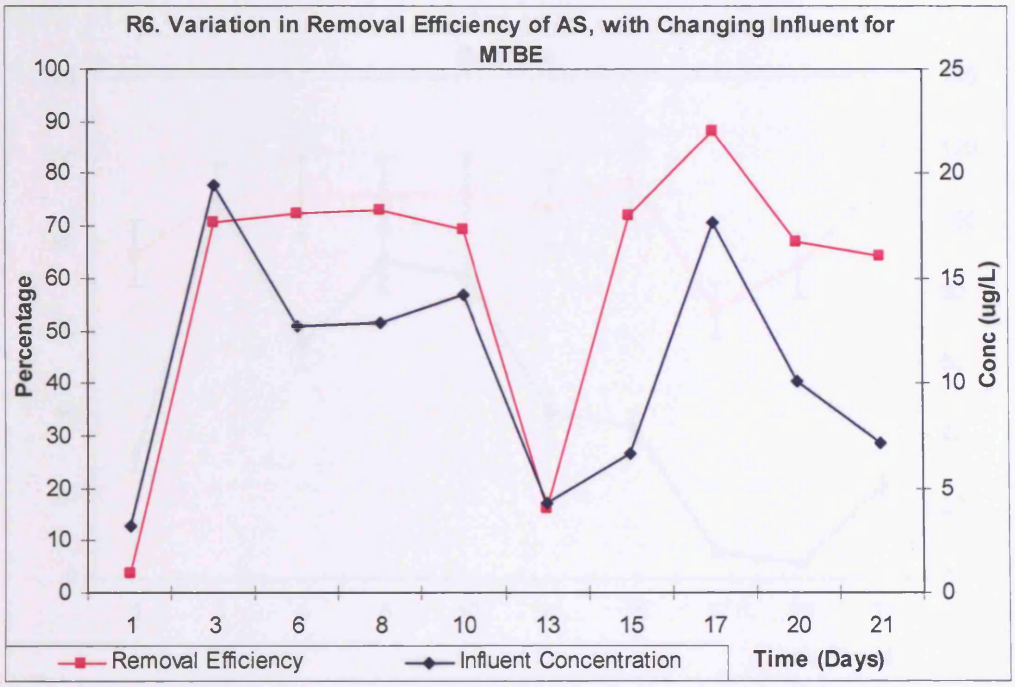


Figure 4.22. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 6.

Run 6 Benzene.

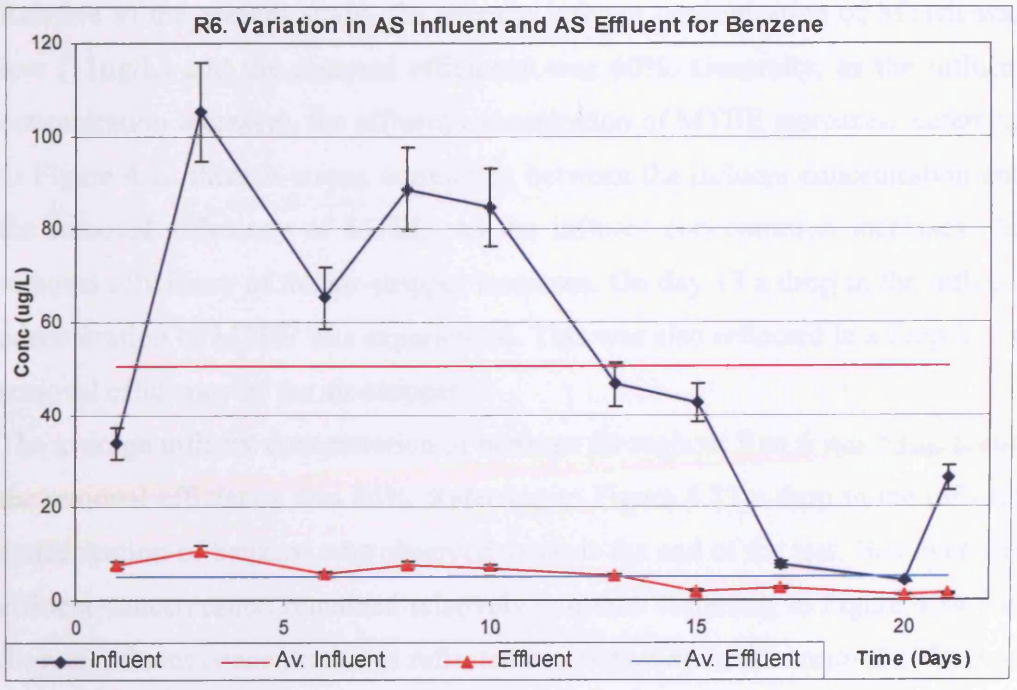


Figure 4.23. Graph to show Influent and Effluent Concentrations of Benzene, during Run 6.

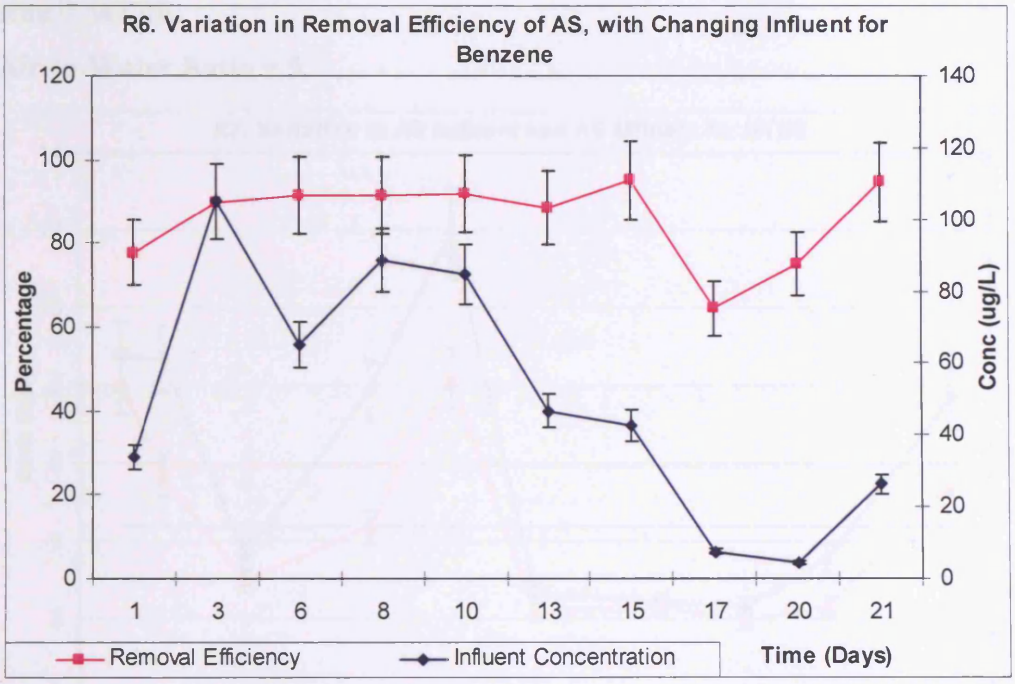


Figure 4.24. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run 6.

Summary.

Relative to the present study, the average influent concentration of MTBE was low (11µg/L) and the removal efficiency was 60%. Generally, as the influent concentration increases, the effluent concentration of MTBE increases. Referring to Figure 4.22 there is strong correlation between the influent concentration and the removal efficiency of MTBE. As the influent concentration increases, the removal efficiency of the air-stripper increases. On day 13 a drop in the influent concentration of MTBE was experienced. This was also reflected in a drop in the removal efficiency of the air-stripper.

The average influent concentration of benzene throughout Run 6 was 53µg/L and the removal efficiency was 85%. Referring to Figure 4.23 a drop in the influent concentration of benzene was observed towards the end of the test. However, the effluent concentration remained relatively constant. Referring to Figure 4.24, the drop in influent concentration is reflected in a reduction in the removal efficiency of the air-stripper.

Run 7 MTBE.

Air-to-Water Ratio = 9.

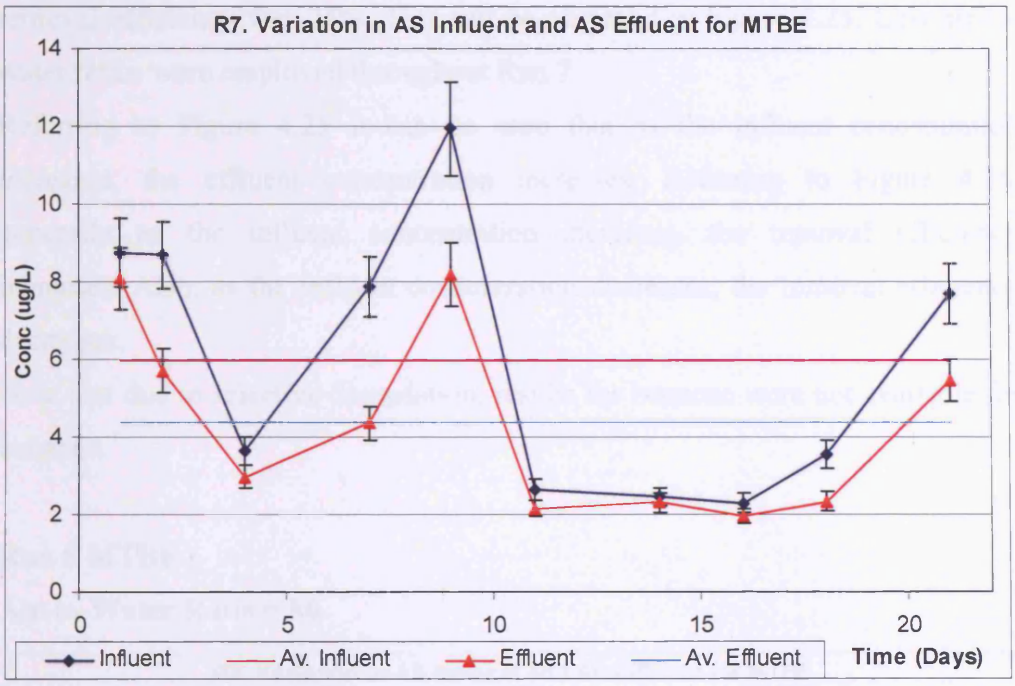


Figure 4.25. Graph to show Influent and Effluent Concentrations of MTBE, during Run 7.

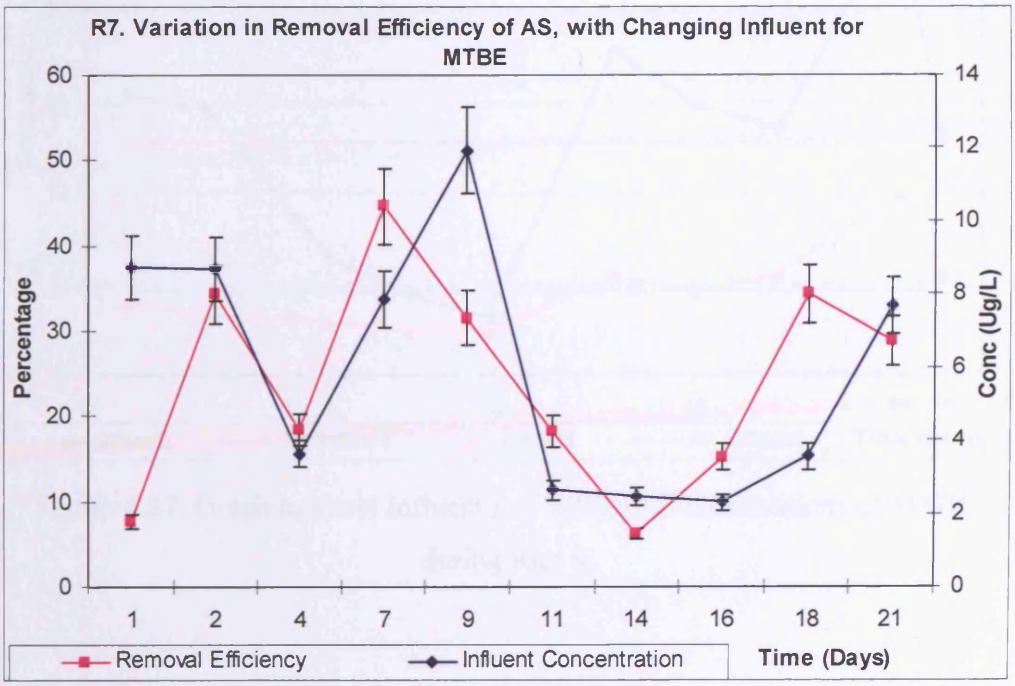


Figure 4.26. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 7.

Summary.

The influent concentration of MTBE throughout Run 7 was low (6μg/L) and the removal efficiency was 24%. This can be observed in Figure 4.25. Low air-to-water ratios were employed throughout Run 7.

Referring to Figure 4.25 it can be seen that as the influent concentration increases, the effluent concentration increases. Referring to Figure 4.26, generally as the influent concentration increases, the removal efficiency increases. Also, as the influent concentration decreases, the removal efficiency decreases.

Note that due to selective degradation, results for benzene were not available for benzene.

Run 8 MTBE.

Air-to-Water Ratio = 86.

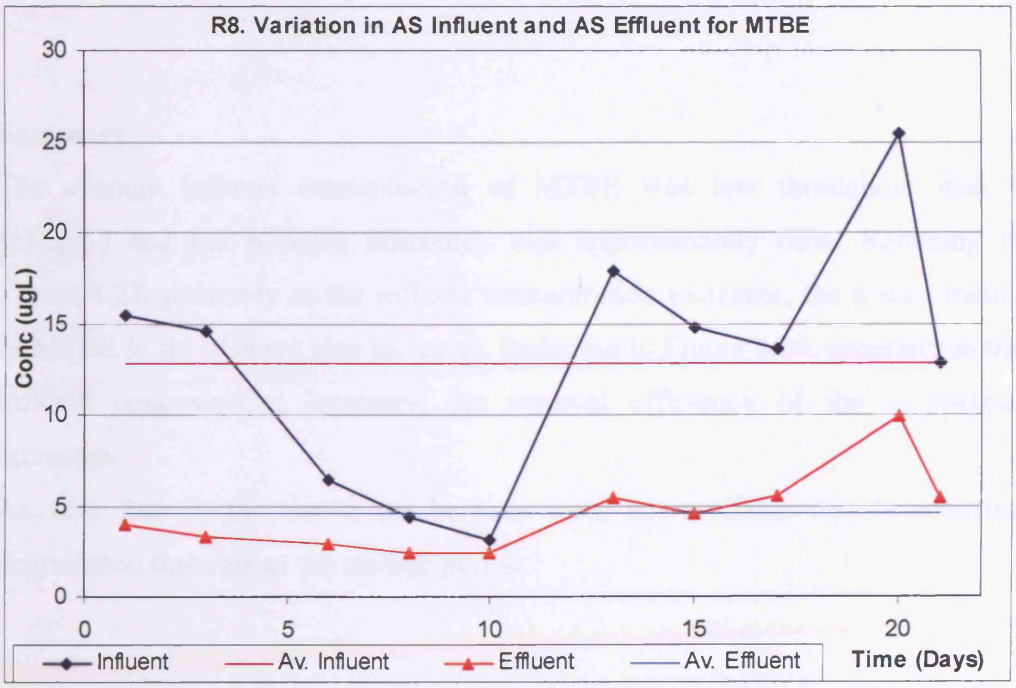


Figure 4.27. Graph to show Influent and Effluent Concentrations of MTBE, during Run 8.

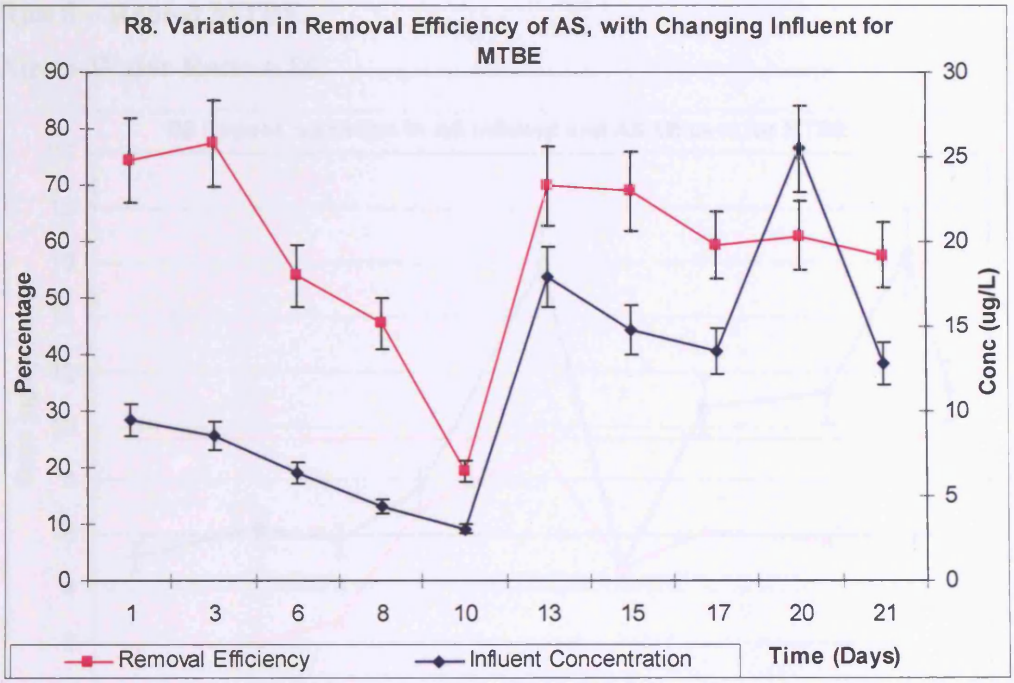


Figure 4.28. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run 8.

Summary.

The average influent concentration of MTBE was low throughout Run 8 (13µg/L) and the removal efficiency was approximately 60%. Referring to Figure 4.27, generally as the influent concentration increases, the concentration of MTBE in the effluent also increases. Referring to Figure 4.28, generally as the influent concentration increases, the removal efficiency of the air-stripper increases.

As with Run 7, the results for benzene were not available due to selective degradation throughout the storage period.

Run 8 – Repeat MTBE.

Air-to-Water Ratio = 86.

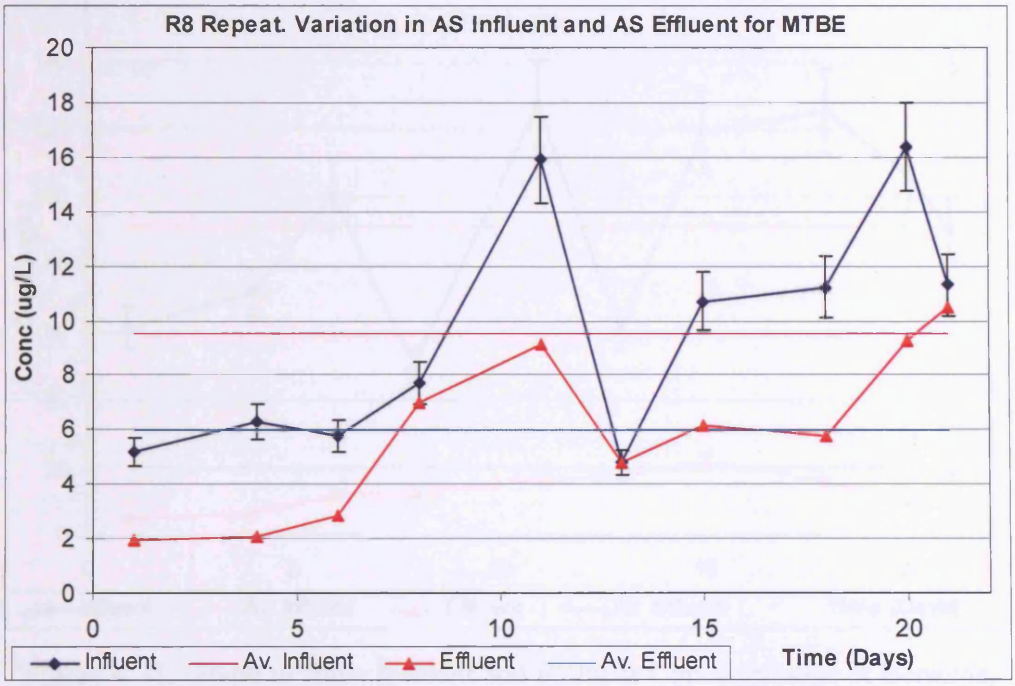


Figure 4.29. Graph to show Influent and Effluent Concentrations of MTBE, during Run – 8 Repeat.

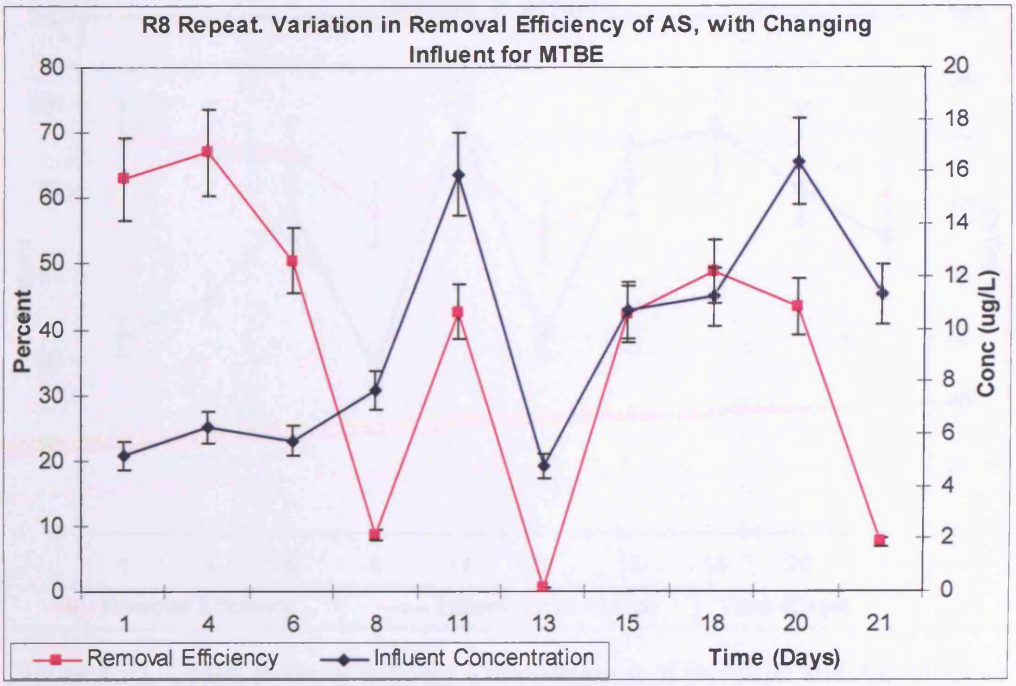


Figure 4.30. Graph to show Influent Concentration of MTBE and Air-Stripper Removal Efficiency during Run – 8 Repeat.

Run – 8 Repeat Benzene.

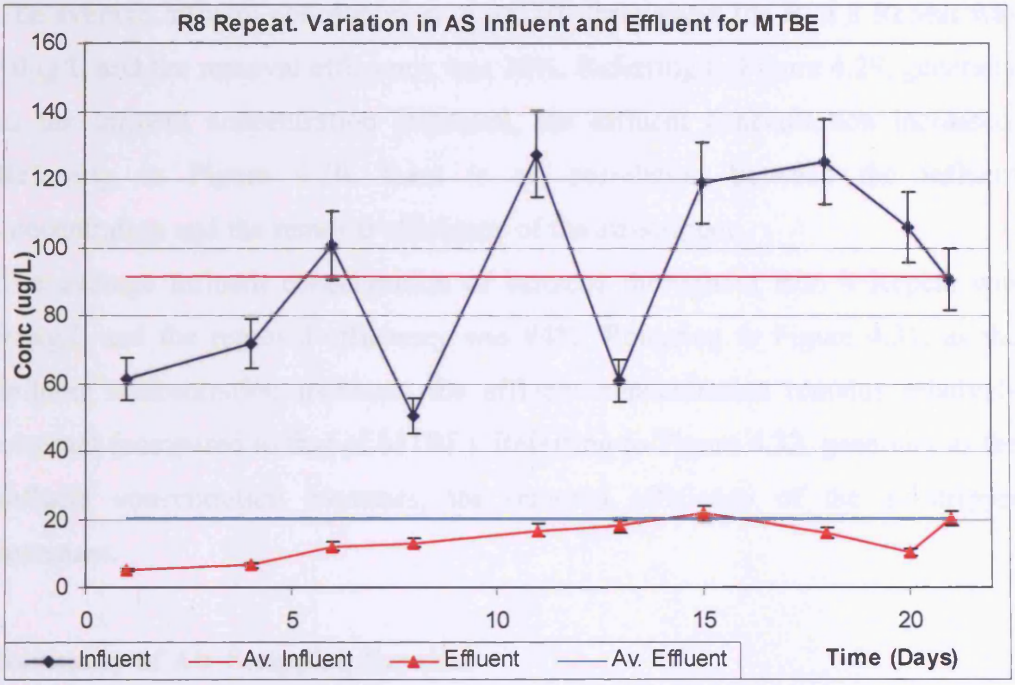


Figure 4.31. Graph to show Influent and Effluent Concentrations of Benzene, during Run – 8 Repeat.

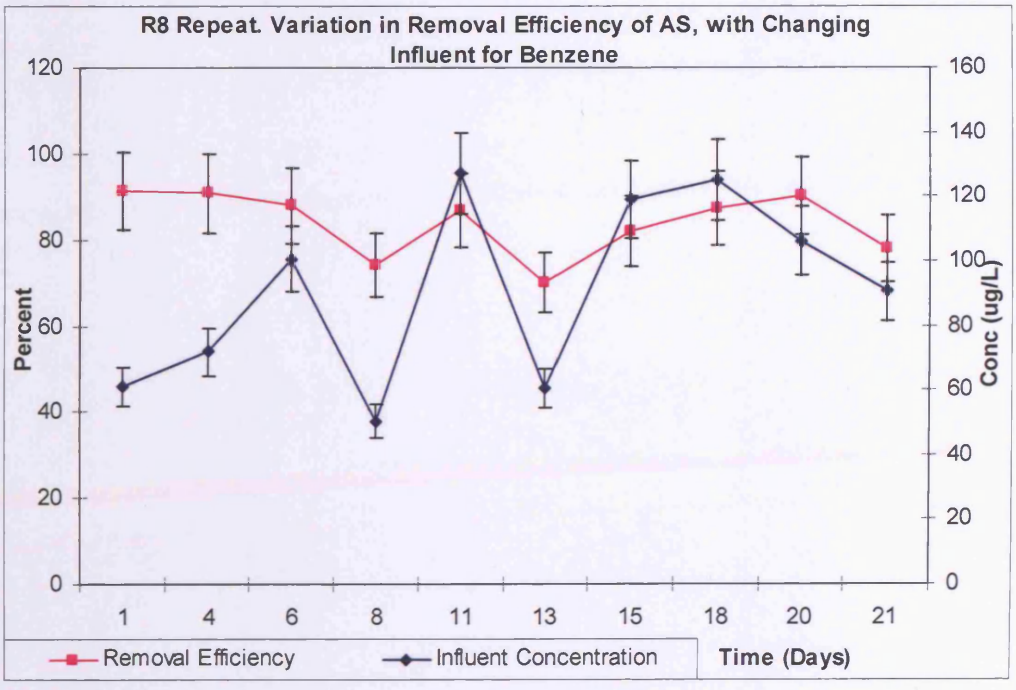


Figure 4.32. Graph to show Influent Concentration of Benzene and Air-Stripper Removal Efficiency during Run – 8 Repeat.

Summary.

The average influent concentration of MTBE throughout the Run 8 Repeat was 10μg/L and the removal efficiency was 39%. Referring to Figure 4.29, generally as the influent concentration increased, the effluent concentration increased. Referring to Figure 4.30, there is no correlation between the influent concentration and the removal efficiency of the air-stripper.

The average influent concentration of benzene throughout Run 8 Repeat was 91μg/L and the removal efficiency was 84%. Referring to Figure 4.31, as the influent concentration increases the effluent concentration remains relatively constant (compared to that of MTBE). Referring to Figure 4.32, generally as the influent concentration increases, the removal efficiency of the air-stripper increases.

Summary of Air-Stripping Results.

Table 4.7 presents the overall air-stripping results. Included in the table is a calculation of the mass transfer coefficient (K_La) based upon the experimental results. The mass transfer coefficient was calculated using equation 1.10.

		Av. Influent (µg/L)	Av. Effluent (µg/L)	Air:water Ratio	Packing Height (m)	ARE%	Ranking	M µg /m^3 h^{-1}	P µg /L	K_La (h)
RUN 1	MTBE	175	84	12	1500	41	3	172	91	1.9
	BENZENE	135	12			90	1	249	123	2.0
RUN 2	MTBE	23	18	12	750	20	5	7.4	5	1.5
	BENZENE	74	16			81	2	90	58	1.6
RUN 3	MTBE	67	6.4	86	1500	89	1	108	60.6	1.8
	BENZENE	28	10			52	4	35	18	1.9
RUN 4	MTBE	163	93	9	750	41	3	112	70	1.6
	BENZENE	164	23			76	3	167	141	1.2
RUN 5	MTBE	53	19	65	750	59	2	67	34	2.0
	BENZENE	30	7.5			74	3	45	22.5	2.0
RUN 6	MTBE	11	3.4	65	1500	60	2	16	7.6	2.1
	BENZENE	51	5.1			85	2	95	45.9	2.1
RUN 7	MTBE	6	4.4	9	1500	24	4	2.5	1.6	1.6
	BENZENE	NDA	NDA			NDA	NDA	NDA	NDA	NDA
RUN 8	MTBE	13	4.6	86	750	60	2	16	8.4	1.9
	BENZENE	NDA	NDA			NDA	NDA	NDA	NDA	NDA
RUN 8 R	MTBE	10	6.4	86	750	39	-	7.2	3.6	2.0
	BENZENE	91	20			84	-	141	71	2.0

Table 4.7. Summary of Air-Stripping Result

Referring to Table 4.7 it can be noted that the average removal efficiency of benzene throughout the experimental period ranged from 52 – 90%. The median benzene ARE% value throughout the experimental trials was 81%. The highest removal efficiency occurred during Run 1 when the influent concentration was high. Note that the air-to-water ratio was low during Run 1 (12) yet a removal efficiency of 90% was achieved. This can be explained in term of the mass transfer coefficient. Referring to equation 1.5 it can be noted that when the concentration gradient is greater (higher influent concentration), the mass transfer of volatile compounds such as benzene will increase.

The lowest ARE% occurred in Run 3 (52%) when the influent concentration was low (28μg/L). Note also that the air-to-water ratio was high (86) and the packing height was high (1500mm). This again suggests that for volatile compounds such as benzene, removal efficiency is dependent upon the concentration difference and hence mass transfer. Referring to Run 1 and 4 it can be noted that the packing height does not impose any significant influence on the ARE%. This concurs with literature in which Roberts *et al* (1985) suggested that the packed height (Z) had relatively little effect on the mass transfer coefficient.

Referring to table 4.7 it can be noted that the ARE% of MTBE throughout the experimental period ranged between 20 – 89%. The median MTBE ARE% value throughout the experimental trials was 41%. The highest ARE% was achieved when the air-to-water ratio was set high (Run 3 – 86). Given that MTBE is known to be less amenable to air-stripping due to its low Henry's Law Constant, it follows that removal efficiency would increase when air-to-water ratios were higher. This trend is repeated throughout the whole of the tests, where it can be noted that removal efficiency is greater when the air-to-water ratios are high.

As with benzene, comparing Runs 1 and 4 suggests that removal efficiency is not dependent on the packing height of the air-stripper.

As expected, the removal efficiency and mass transfer of the air-stripping system was generally greater for benzene than it was for MTBE, regardless of the air-to-water ratio. This can be attributed to the physiochemical nature of the respective compounds. Benzene is known to be more amenable to air-stripping because of its higher Henry's Law constant and lower solubility.

The mass transfer coefficients calculated using the experimental data sets were found to be of the same order of magnitude as those derived by the Onda method

(Section 3.2.1.2 of Chapter 3). This shows good correlation between the Onda method (based upon theoretical input parameters) and the results gained through experimentation.

The influence of the variable influent concentration on the performance of the air-stripping process is notable throughout the results. Generally, as the influent concentration of benzene varies, the effluent concentration remains relatively stable. With respect to MTBE, as the influent concentration increases, the concentration of MTBE in the effluent also increases.

Generally throughout the results, an increase in the effluent concentration corresponds to an increase in the efficiency of the air-stripping process.

4.3. Adsorption Column Results.

Variable Influent Concentration.

It was suggested in Section 3.2.7 of Chapter 3 that the influent concentration would vary throughout the duration of each test. The variable influent concentration can be observed in the air-stripping results (4.2).

Since breakthrough and total (or ultimate) capacity of the carbon is determined by the equilibrium of the adsorption process, the variable influent concentration was likely to affect the adsorption column results.

The influent concentration to the adsorption column was both affected by the influent concentration entering the air-stripper and the efficiency of the air-stripping process relative to the parameters used within each test. In order to present the tabulated adsorption column results independently from the influent concentration, capacity until breakthrough and capacity for the duration of the test was calculated.

The mass of substance adsorbed at any given point throughout the duration of the experiment can be expressed graphically if the time to component breakthrough (X-axis) is converted to volume of water treated. Referring to figure 4.33, the orange shaded area is directly proportional to the mass of benzene adsorbed.

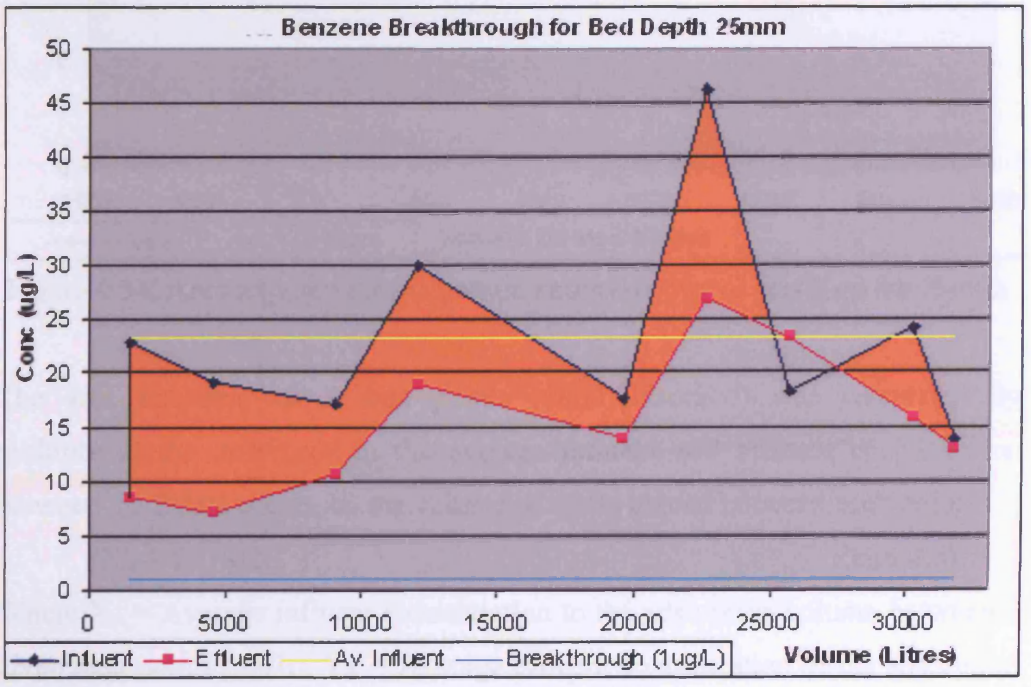


Figure 4.33. Mass of Benzene Adsorbed for Duration of Test.

At any specific point the mass adsorbed by the GAC was calculated by;

$$(X\text{-}Y) \times Z \qquad \textbf{(eqn 4.2)}$$

Where X = Influent to adsorption column (µg/L), Y = Effluent of adsorption column (at a given bed depth) (µg/L) and Z = Volume of water treated a specific time (litres). Note that the actual concentration between time zero and the first data point is likely to vary; hence the calculation should be regarded as an indication only.

Figure 4.34 details the area required for integration between 2 - data points (excluding those between time zero and the first data point), where the orange shaded area is directly proportional to the mass adsorbed by the carbon.

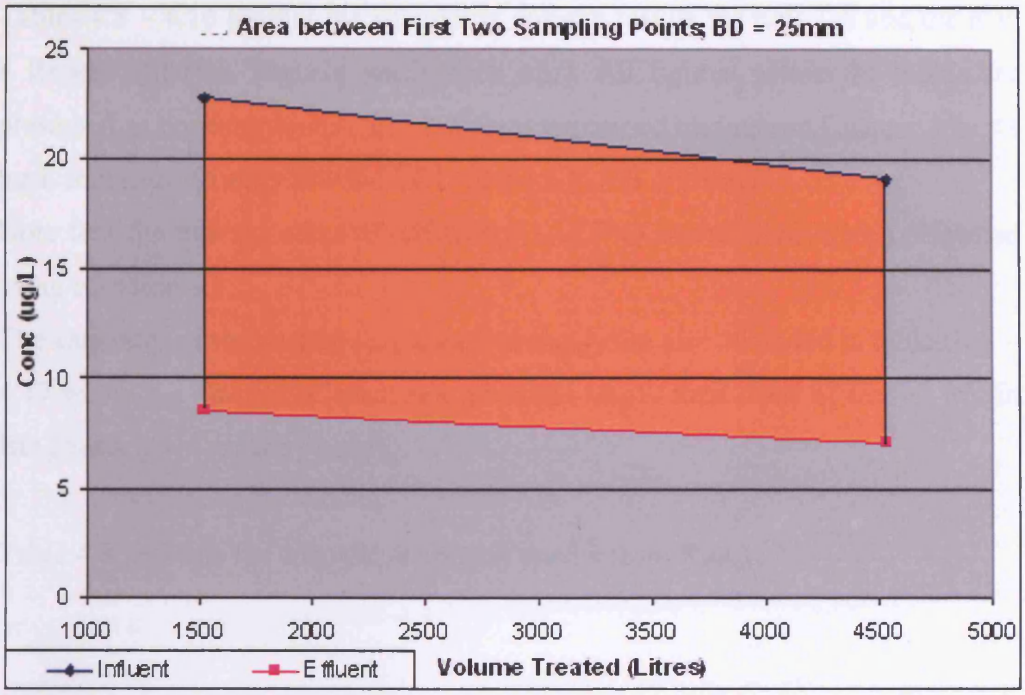


Figure 4.34. Area required for integration between points 1 and 2 on the X-axis.

The area between the 2 data points (mass adsorbed) was calculated by multiplying the difference in the average influent and effluent concentration between the 2 data points, by the volume of water treated between each point;

$$(X_A - Y_A) \times Z_D \qquad \textbf{(eqn 4.3)}$$

Where X_A = Average influent concentration to the adsorption column between 2 given data points (µg/L), Y_A = Average effluent concentration of the adsorption column between 2 given data points (µg/L) and Z_D = Volume of water treated between 2 data points (litres).

In order to calculate the total mass adsorbed between time zero and day 3, the mass calculated for day 1 was added to the mass adsorbed between day 1 and 3.
Referring to Figure 4.33, it can be noted that towards the latter stages of the example test, the influent concentration is less than the effluent concentration. It is possible that since the ability of the carbon to adsorb dissolved compounds is determined by the equilibrium of the adsorption process, that desorption of the adsorbate back into solution can occur as the system approaches equilibrium. For the purpose of the adsorption column results, when calculating the capacity of the carbon, if desorption occurred the amount desorbed was subtracted from the overall capacity.
Tables 4.8 – 4.16 present the adsorption column results for runs 1-8 and the Run 8 Repeat test (the Taguchi verification test). All figures within the tables are presented as concentrations (μg/L). Values expressed throughout Chapter 4 as <1 μg/L represent those below the LOD of the GC-MS apparatus.
Note that the average removal efficiency (ARE%) calculations were performed using equation 4.1.
The capacitiy of the carbon (expressed as mg/g) are also included in tables 4.8 – 4.17 where the amount of substance adsorbed (mg) / total mass of carbon within BD 25mm (g) = capacity (mg/g).

Table 4.8 presents the adsorption column results from Run 1.

RUN 1		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	108	64	36	NDA
	BENZENE	12	<1	<1	NDA
Day 4	MTBE	71	63	61	NDA
	BENZENE	7.4	1.3	<1	NDA
Day 6	MTBE	83	80	83	NDA
	BENZENE	11	2.9	1.1	NDA
Day 8	MTBE	47	52	54	NDA
	BENZENE	7.3	3.9	1.6	NDA
Day 12	MTBE	59	68	65	NDA
	BENZENE	7.2	4.2	1.1	NDA
Day 14	MTBE	139	133	131	NDA
	BENZENE	20	10	6.7	NDA
Day 16	MTBE	128	90	95	NDA
	BENZENE	19	7.6	4.6	NDA
Day 19	MTBE	96	58	57	NDA
	BENZENE	13	4.8	3.0	NDA
Day 21	MTBE	110	109	103	NDA
	BENZENE	15	9	5.5	NDA
MTBE	Average	89	80	76	NDA
	ARE%		14	24	NDA
	BT (Days)		1	1	NDA
	BT (BV)		7714	3847	NDA
	Mass adsorbed until BT (g)		0.008	0.049	NDA
	Capacity until BT (mg/g)		0.09		
	Total mass adsorbed (g)		0.297	0.41	NDA
	Total carbon capacity (mg/g)		3.45		
Benzene	Average	13	4.9	2.7	NDA
	ARE%		62	82	NDA
	BT (Days)		4	6	NDA
	BT (BV)		30857	23084	NDA
	Mass adsorbed until BT (g)		0.059	0.088	NDA
	Capacity until BT (mg/g)		0.69		
	Total mass adsorbed (g)		0.234	0.303	NDA
	Total carbon capacity (mg/g)		2.72		

Table 4.8. Adsorption Column Results from Run 1.

Table 4.9 presents the adsorption column results from Run 2.

RUN 2		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	22	19	16	16
	BENZENE	21	6.9	2.3	NDA
Day 4	MTBE	12	10	9.7	NDA
	BENZENE	12	4.0	1.8	NDA
Day 6	MTBE	13	13	13	13
	BENZENE	13	9.2	5.2	2.0
Day 8	MTBE	25	22	20	NDA
	BENZENE	18	12	6.0	NDA
Day 11	MTBE	14	14	13	NDA
	BENZENE	10	10	5.9	NDA
Day 13	MTBE	14	13	13	13
	BENZENE	12	9.4	6.3	1.3
Day 15	MTBE	21	20	20	NDA
	BENZENE	13	13	10	NDA
Day 19	MTBE	20	19	18	17
	BENZENE	29	19	13	4.0
Day 21	MTBE	18	16	16	15
	BENZENE	23	16	13	5.6
Day 25	MTBE	21	19	18	17
	BENZENE	13	12	9.6	5.0
Day 26	MTBE	21	20	20	19
	BENZENE	14	12	9.9	5.4
MTBE	Average	18	17	16	NDA
	ARE%		9	14	NDA
	BT (Days)		1	1	NDA
	BT (BV)		7714	3847	NDA
	Mass adsorbed until BT (g)		0.001	0.009	NDA
	Capacity until BT (mg/g)		0.05		
	Total mass adsorbed (g)		0.052	0.088	NDA
	Total carbon capacity (mg/g)		0.61		
Benzene	Average	16	11	7.5	NDA
	ARE%		9	14	NDA
	BT (Days)		1	1	NDA
	BT (BV)		7714	3847	NDA
	Mass adsorbed until BT (g)		0.021	0.028	NDA
	Capacity until BT (mg/g)		0.25		
	Total mass adsorbed (g)		0.206	0.352	NDA
	Total carbon capacity (mg/g)		2.4		

Table 4.9. Adsorption Column Results from Run 2.

Table 4.10 presents the adsorption column results from Run 3.

RUN 3		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	5.3	4.9	2.3	<1
	BENZENE	10	<1	<1	<1
Day 3	MTBE	6.9	4.4	3.4	<1
	BENZENE	16	<1	<1	<1
Day 6	MTBE	4.1	4.9	5.9	9.2
	BENZENE	10	<1	<1	<1
Day 8	MTBE	9.5	9.2	9.5	3.1
	BENZENE	19	<1	<1	<1
Day 11	MTBE	4.8	5.5	4.0	4.2
	BENZENE	5.6	5.7	1.5	1.4
Day 13	MTBE	4.5	4.8	5.5	4.9
	BENZENE	5.1	1.6	1.5	1.1
Day 15	MTBE	15	11	11	9.2
	BENZENE	4.3	2.8	2.8	<1
Day 18	MTBE	5.1	5.6	4.9	4.7
	BENZENE	8.8	3.1	2.7	<1
Day 20	MTBE	3.4	4.1	3.7	3.2
	BENZENE	8.0	7.8	2.6	<1
Day 21	MTBE	5.1	4.7	3.9	3.2
	BENZENE	11	8.6	2.7	<1
MTBE	Average	6.4	6.0	5.4	4.2
	ARE%		15	25	46
	BT (Days)		1	6	6
	BT (BV)		7714	23048	6622
	Mass adsorbed until BT (g)		0.001	0.018	0.031
	Capacity until BT (mg/g)		0.005		
	Total mass adsorbed (g)		0.017	0.032	0.071
	Total carbon capacity (mg/g)		0.14		
Benzene	Average	9.8	3.0	1.4	<1
	ARE%		66	79	95
	BT (Days)		11	11	11
	BT (BV)		84857	42321	12140
	Mass adsorbed until BT (g)		0.203	0.213	0.213
	Capacity until BT (mg/g)		1.64		
	Total mass adsorbed (g)		0.243	0.277	0.307
	Total carbon capacity (mg/g)		1.96		

Table 4.10. Adsorption Column Results from Run 3.

Table 4.11 presents the adsorption column results from Run 4.

RUN 4		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	107	107	92	49
	BENZENE	23	8.5	1.2	<1
Day 3	MTBE	78	87	78	56
	BENZENE	19	7.1	<1	<1
Day 6	MTBE	136	115	100	71
	BENZENE	17	11	3.3	<1
Day 8	MTBE	137	120	107	2.9
	BENZENE	30	19	7.5	<1
Day 13	MTBE	58	57	63	67
	BENZENE	18	14	7.6	<1
Day 15	MTBE	158	125	114	105
	BENZENE	46	27	16	1.8
Day 17	MTBE	83	102	98	92
	BENZENE	18	23	15	2.1
Day 20	MTBE	55	46	45	52
	BENZENE	24	16	12	2.1
Day 21	MTBE	28	36	36	40
	BENZENE	14	13	9.4	2.0
MTBE	Average	93	88.0	81	68
	ARE%		11	22	45
	BT (Days)		1	1	1
	BT (BV)		7714	3847	1104
	Mass adsorbed until BT (g)		0.002	0.042	0.089
	Capacity until BT (mg/g)		0.01		
	Total mass adsorbed (g)		0.185	0.414	0.903
	Total carbon capacity (mg/g)		1.49		
Benzene	Average	23	15	8.0	<1
	ARE%		31	63	96
	BT (Days)		1	1	15
	BT (BV)		7714	3847	16554
	Mass adsorbed until BT (g)		0.022	0.033	0.526
	Capacity until BT (mg/g)		0.18		
	Total mass adsorbed (g)		0.254	0.505	0.729
	Total carbon capacity (mg/g)		2.05		

Table 4.11. Adsorption Column Results from Run 4.

Table 4.12 presents the adsorption column results from Run 5.

RUN 5		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 2	MTBE	22	13	9.3	<1
	BENZENE	9.3	4.9	3.8	<1
Day 4	MTBE	26	18	14	5.7
	BENZENE	10	5.7	4.1	<1
Day 6	MTBE	20	17	12	5.1
	BENZENE	8.0	4.8	3.8	<1
Day 9	MTBE	18	13	11	10
	BENZENE	7.6	5.6	4.2	<1
Day 11	MTBE	11	11	11	10
	BENZENE	5.7	5.4	4.3	<1
Day 14	MTBE	12	11	11	11
	BENZENE	6.4	5.4	3.9	<1
Day 16	MTBE	23	21	19	18
	BENZENE	7.4	7.5	5.6	3.4
Day 18	MTBE	21	18	17	16
	BENZENE	6.7	6.2	4.5	3.3
Day 21	MTBE	17	14	13	14
	BENZENE	5.8	5.9	4.6	3.5
MTBE	Average	19	15.0	13	10
	ARE%		17	28	41
	BT (Days)		2	2	4
	BT (BV)		15429	7695	4415
	Mass adsorbed until BT (g)		0.027	0.038	0.13
	Capacity until BT (mg/g)		0.32		
	Total mass adsorbed (g)		0.125	0.198	0.309
	Total carbon capacity (mg/g)		1.46		
Benzene	Average	7.5	5.7	4.3	1.1
	ARE%		27	40	8.3
	BT (Days)		2	2	16
	BT (BV)		15429	7695	17658
	Mass adsorbed until BT (g)		0.013	0.017	0.185
	Capacity until BT (mg/g)		0.15		
	Total mass adsorbed (g)		0.061	0.105	0.209
	Total carbon capacity (mg/g)		0.7		

Table 4.12. Adsorption Column Results from Run 5.

Table 4.13 presents the adsorption column results from Run 6.

RUN 6		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	3.1	2.6	1.8	<1
	BENZENE	7.6	1.1	<1	<1
Day 3	MTBE	5.7	4.5	3.2	<1
	BENZENE	11	2.6	<1	<1
Day 6	MTBE	3.5	3.5	2.5	1.4
	BENZENE	5.6	2.2	<1	<1
Day 8	MTBE	3.5	4.1	3.3	2
	BENZENE	7.5	4.1	1.5	<1
Day 10	MTBE	4.4	3.5	3.5	2.5
	BENZENE	7.0	3.8	1.7	<1
Day 13	MTBE	3.6	3.1	2.7	2.3
	BENZENE	5.3	2.5	1.4	<1
Day 15	MTBE	1.9	2.0	2.0	1.8
	BENZENE	2.1	<1	<1	<1
Day 17	MTBE	2.1	2.1	1.9	1.8
	BENZENE	2.6	1.6	1.1	<1
Day 20	MTBE	3.4	3.2	2.9	2.2
	BENZENE	1.1	1.1	<1	<1
Day 21	MTBE	2.5	2.9	2.8	2.4
	BENZENE	1.4	1.2	1.5	<1
MTBE	Average	3.4	3.2	2.7	1.7
	ARE%		11	23	43
	BT (Days)		NBT	NBT	NBT
	BT (BV)		NBT	NBT	NBT
	Mass adsorbed until BT (g)		0.002	0.042	0.089
	Capacity until BT (mg/g)		0.09		
	Total mass adsorbed (g)		0.185	0.414	0.903
	Total carbon capacity (mg/g)		0.09		
Benzene	Average	23	15	8.0	<1
	ARE%		31	63	96
	BT (Days)		1	1	15
	BT (BV)		7714	3847	16554
	Mass adsorbed until BT (g)		0.022	0.033	0.526
	Capacity until BT (mg/g)		0.11		
	Total mass adsorbed (g)		0.254	0.505	0.729
	Total carbon capacity (mg/g)		1.25		

Table 4.13. Adsorption Column Results from Run 6.

Table 4.14 presents the adsorption column results from Run 7.

RUN 7		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	8.1	5.8	4.4	1.0
	BENZENE	NDA	NDA	NDA	NDA
Day 2	MTBE	5.7	5.5	5.1	2.5
	BENZENE	NDA	NDA	NDA	NDA
Day 3	MTBE	3.0	3.0	2.8	2.2
	BENZENE	NDA	NDA	NDA	NDA
Day 7	MTBE	4.4	4.1	3.3	2.5
	BENZENE	NDA	NDA	NDA	NDA
Day 9	MTBE	8.2	1.5	1.9	1.3
	BENZENE	NDA	NDA	NDA	NDA
Day 11	MTBE	2.2	2.0	1.9	1.5
	BENZENE	NDA	NDA	NDA	NDA
Day 14	MTBE	2.3	2.1	1.9	1.6
	BENZENE	NDA	NDA	NDA	NDA
Day 16	MTBE	2.0	1.9	1.8	1.7
	BENZENE	NDA	NDA	NDA	NDA
Day 18	MTBE	2.3	2.7	2.5	2.1
	BENZENE	NDA	NDA	NDA	NDA
Day 21	MTBE	5.5	3.0	2.9	2.3
	BENZENE	NDA	NDA	NDA	NDA
MTBE	Average	4.4	3.1	2.9	1.8
	ARE%		21	27	44
	BT (Days)		1	2	NBT
	BT (BV)		7714	7695	NBT
	Mass adsorbed until BT (g)		0.004	0.009	NBT
	Capacity until BT (mg/g)		0.03		
	Total mass adsorbed (g)		0.033	0.041	0.07
	Total carbon capacity (mg/g)		0.26		

Table 4.14. Adsorption Column Results from Run 7.

Table 4.15 presents the adsorption column results from Run 8.

RUN 8		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	4.0	2.8	2.4	<1
	BENZENE	NDA	NDA	NDA	NDA
Day 3	MTBE	3.3	2.6	2.3	1.3
	BENZENE	NDA	NDA	NDA	NDA
Day 6	MTBE	2.9	2.2	2.1	1.5
	BENZENE	NDA	NDA	NDA	NDA
Day 8	MTBE	2.4	2.0	2.4	1.8
	BENZENE	NDA	NDA	NDA	NDA
Day 10	MTBE	2.5	2.1	2.0	1.8
	BENZENE	NDA	NDA	NDA	NDA
Day 13	MTBE	5.4	5.7	5.5	4.2
	BENZENE	NDA	NDA	NDA	NDA
Day 15	MTBE	4.6	4.6	4.5	3.4
	BENZENE	NDA	NDA	NDA	NDA
Day 17	MTBE	5.5	4.5	4.6	3.8
	BENZENE	NDA	NDA	NDA	NDA
Day 20	MTBE	9.9	8.5	7.2	5.3
	BENZENE	NDA	NDA	NDA	NDA
Day 21	MTBE	5.4	5.5	5.4	5.3
	BENZENE	NDA	NDA	NDA	NDA
MTBE	Average	4.6	4.1	3.8	2.8
	ARE%		20	19	37
	BT (Days)		13	13	20
	BT (BV)		100286	50015	22073
	Mass adsorbed until BT (g)		0.011	0.013	0.054
	Capacity until BT (mg/g)		0.09		
	Total mass adsorbed (g)		0.018	0.025	0.058
	Total carbon capacity (mg/g)		0.15		

Table 4.15. Adsorption Column Results from Run 8.

Table 4.16 presents the adsorption column results from Run – 8 Repeat.

Run 8 Repeat		Influent (ug/L)	Effluent (ug/L) BD 25mm	Effluent (ug/L) BD 50mm	Effluent (ug/L) BD 175mm
Day 1	MTBE	2.2	1.9	1.1	1.1
	BENZENE	5.3	<1	<1	<1
Day 4	MTBE	2.1	2.0	1.9	1.4
	BENZENE	6.6	<1	<1	<1
Day 6	MTBE	2.8	2.4	2.4	1.8
	BENZENE	12	2.5	<1	<1
Day 8	MTBE	8.6	7.0	8.4	7.9
	BENZENE	13	11	6.5	5.0
Day 11	MTBE	9.1	8.7	8.5	7.7
	BENZENE	17	9.4	6.2	5.0
Day 13	MTBE	6.0	4.8	5.6	5.2
	BENZENE	18	10	7.0	5.5
Day 15	MTBE	6.2	5.9	5.8	5.4
	BENZENE	22	12	7.5	5.5
Day 18	MTBE	6.3	5.8	5.7	5.4
	BENZENE	16	15	9.2	5.5
Day 20	MTBE	10	9.3	5.1	8.1
	BENZENE	10	12	8.0	5.5
Day 21	MTBE	10	9.7	9.8	16
	BENZENE	20	11	7.1	5.5
MTBE	Average	6.4	5.7	4.9	5.2
	ARE%		7	24	29
	BT (Days)		8	8	8
	BT (BV)				
	Mass adsorbed until BT (g)		0.005	0.006	0.011
	Capacity until BT (mg/g)				
	Total mass adsorbed (g)		0.019	0.29	0.033
	Total carbon capacity (mg/g)				
Benzene	Average	14	8.3	5.2	3.8
	ARE%		45	67	76
	BT (Days)		6	8	8
	BT (BV)				
	Mass adsorbed until BT (g)		0.059	0.091	0.093
	Capacity until BT (mg/g)				
	Total mass adsorbed (g)		0.181	0.277	0.32
	Total carbon capacity (mg/g)				

Table 4.16. Adsorption Column Results from Run – 8 Repeat.

The following section presents the adsorption column results in graphical form. As discussed previously in section 4.2, the influent concentration varied throughout each test. Since the adsorption process is essentially an equilibrium, the variable influent concentration is likely to affect the adsorption characteristics of GAC and hence affect the results.

Throughout literature, graphical adsorption results are usually expressed as the fraction of component passing through the adsorbent versus time (Lin and Huang, 1999, Shih *et al*, 2003). This is expressed as C/C_0 where C = concentration of adsorbate in the effluent and C_0 = concentration of adsorbate in the influent. Expressing adsorption column results in this manner takes into account the variable influent concentration from the results.

Run 1 MTBE.

F400 Carbon.

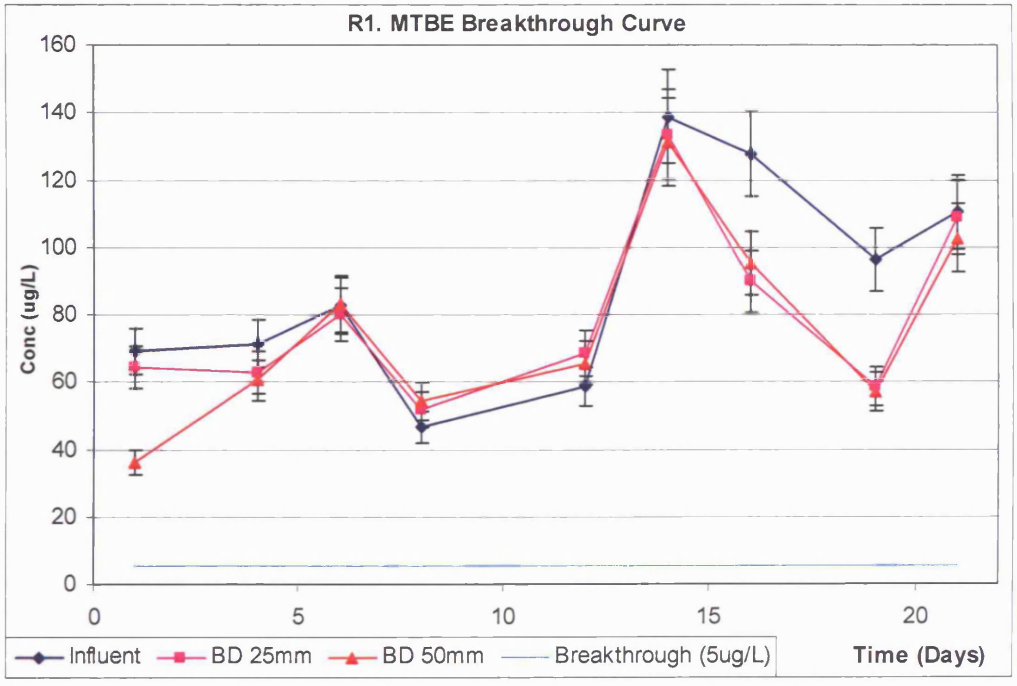


Figure 4.35. Adsorption Column Breakthrough Curve for MTBE, during Run 1.

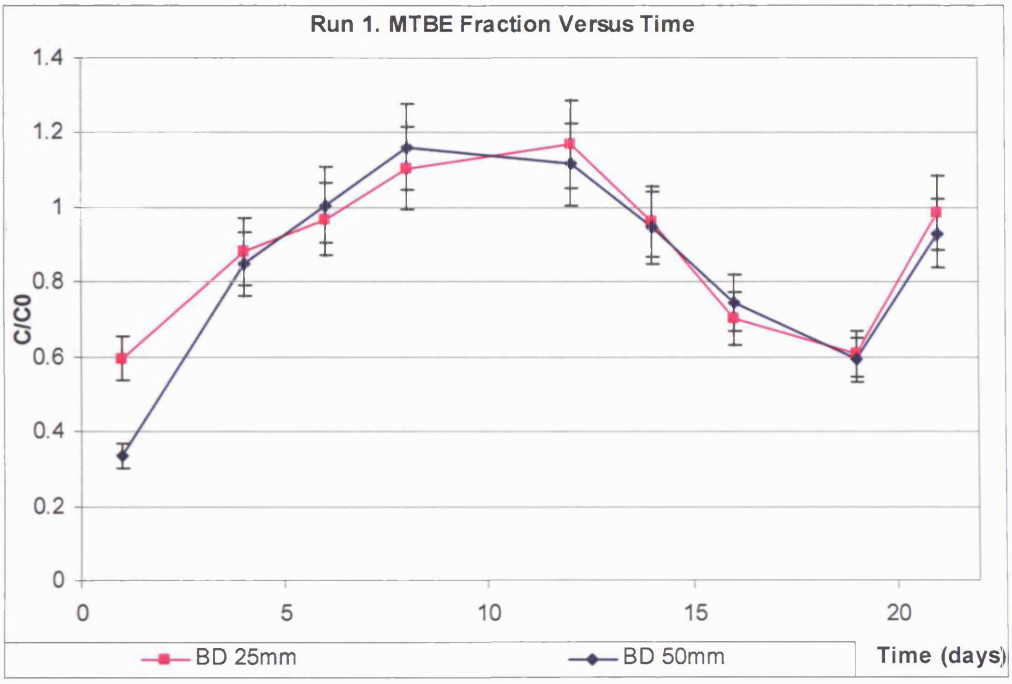


Figure 4.36. MTBE Fraction versus Time during Run 1.

Run 1 Benzene.

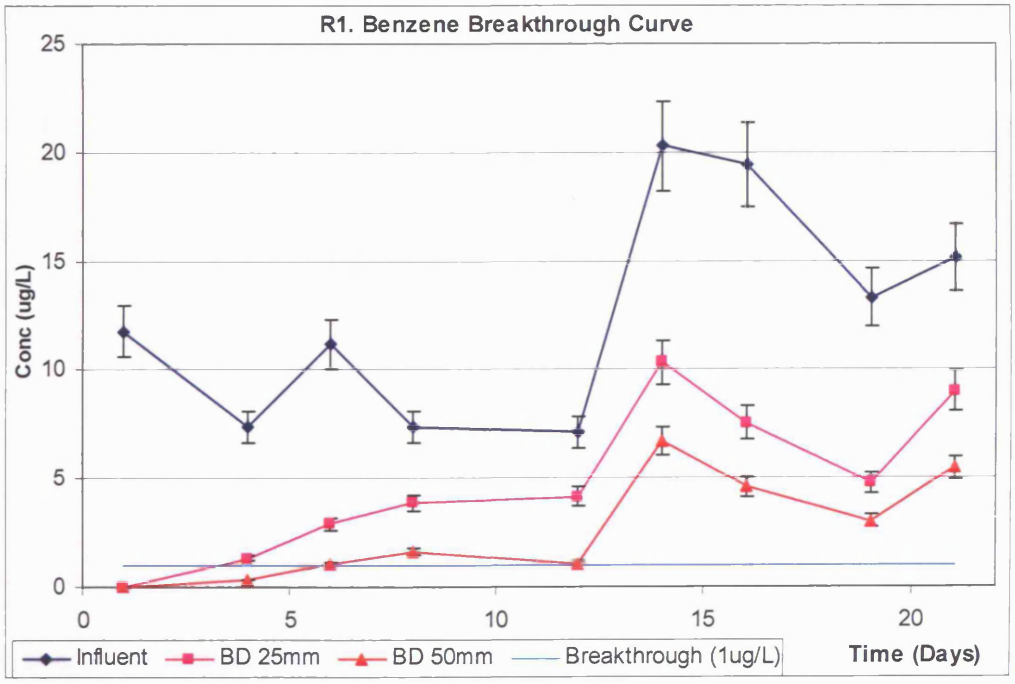


Figure 4.37. Adsorption Column Breakthrough Curve for Benzene, during Run 1.

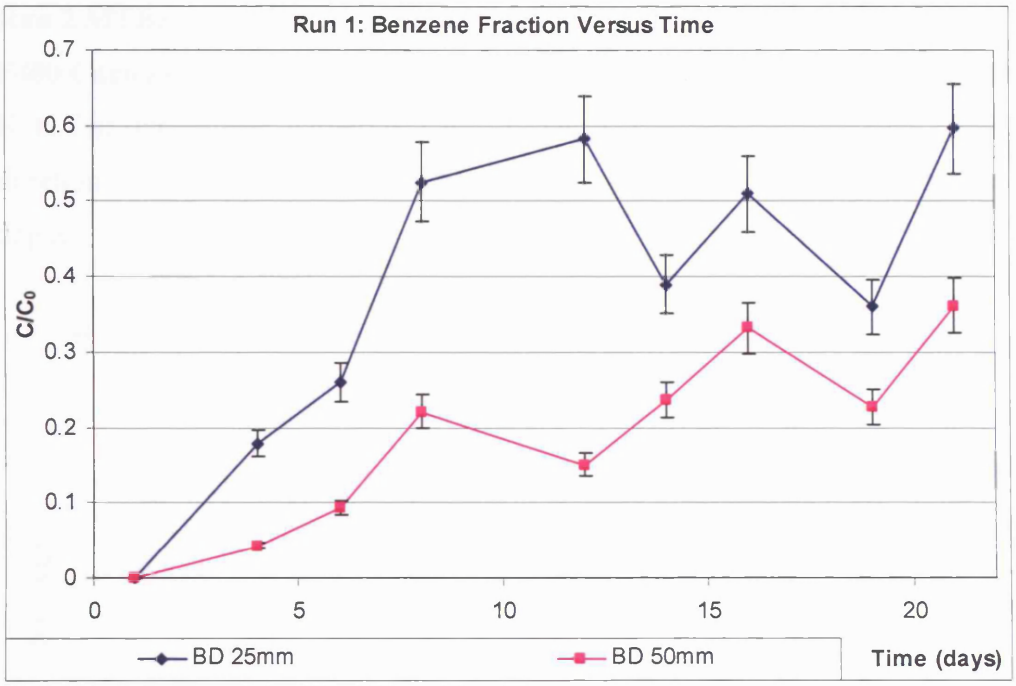


Figure 4.38. Benzene Fraction versus Time during Run 1.

Summary.

The average influent concentration for MTBE throughout Run 1 was 89µg/L. The ARE% for bed depths 25 and 50mm was 14 and 24% respectively. Referring to Figure 4.35 as the influent concentration increased, the concentration of MTBE in the effluent also increased. The graphs presented in Figures 4.35 and 4.36 do not show typical breakthrough curves for adsorption media. This was most likely caused by the variable influent concentration. The remediation target for MTBE was not achieved at any point throughout the tests.

With respect to benzene, the average influent concentration was 13µg/L. The ARE% for bed depths 25 and 50mm was 62 and 82% respectively. As with MTBE, as the influent concentration varied, so did the effluent concentration of benzene. Referring to Figures 4.37 and 4.38, the results exhibited characteristics closer to that of a typical breakthrough curve. The remediation target for benzene was achieved for bed depths 25 and 50mm for 4 and 6-days respectively.

Run 2 MTBE.

F400 Carbon.

Note that during Run 2 samples were not taken from bed depth 175mm for the duration of the test, hence it was not possible to generate a curve for this bed depth.

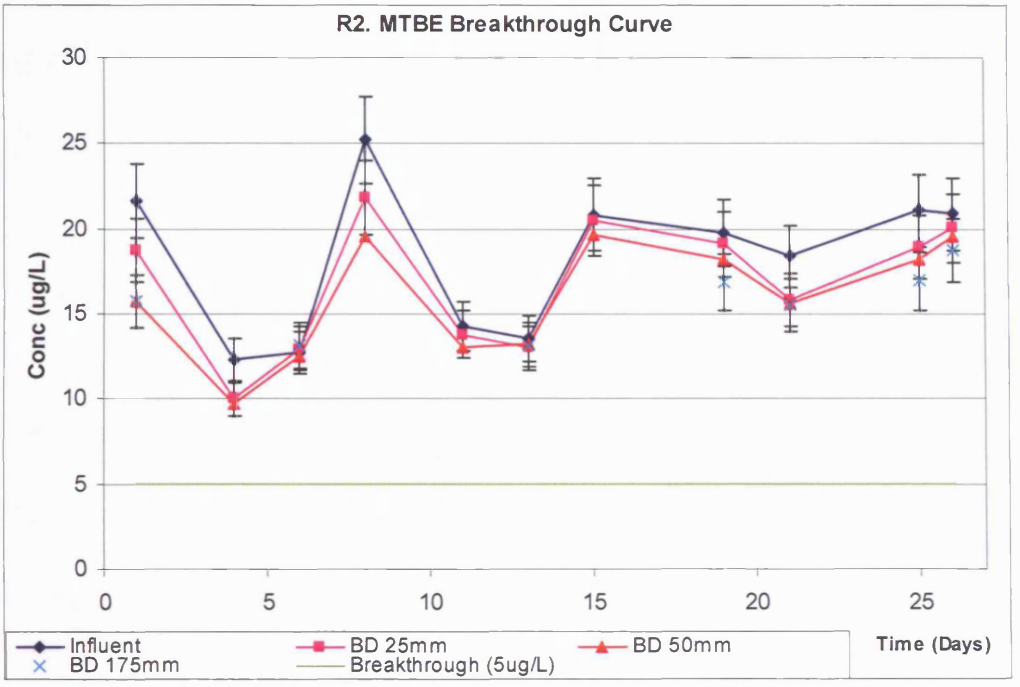


Figure 4.39. Adsorption Column Breakthrough Curve for MTBE, during Run 2.

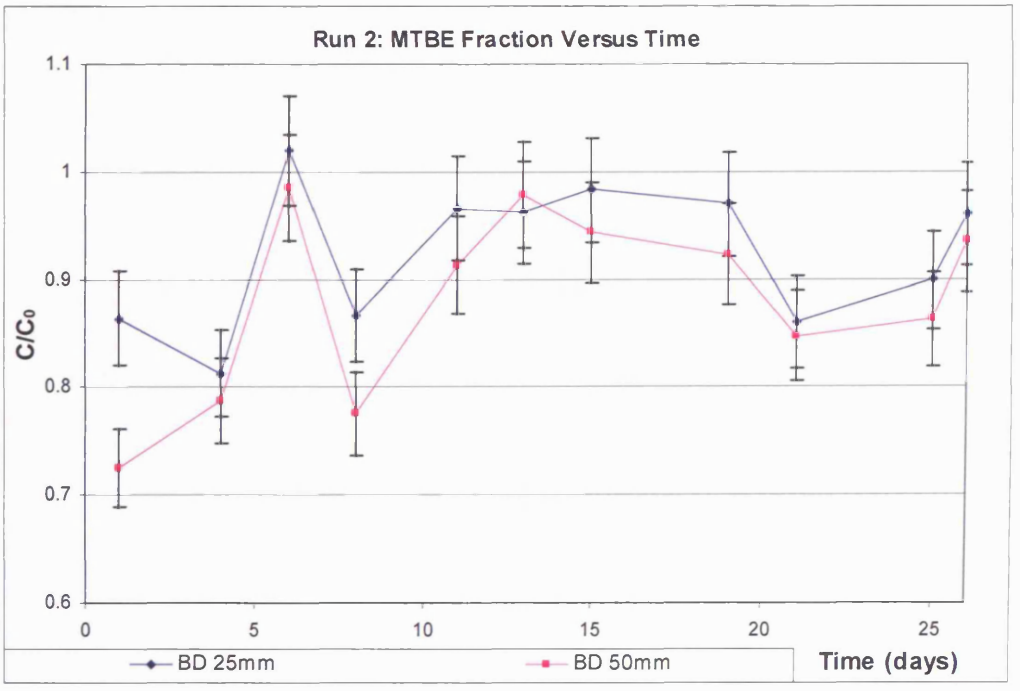


Figure 4.40. MTBE Fraction versus Time during Run 2.

Run 2 Benzene.

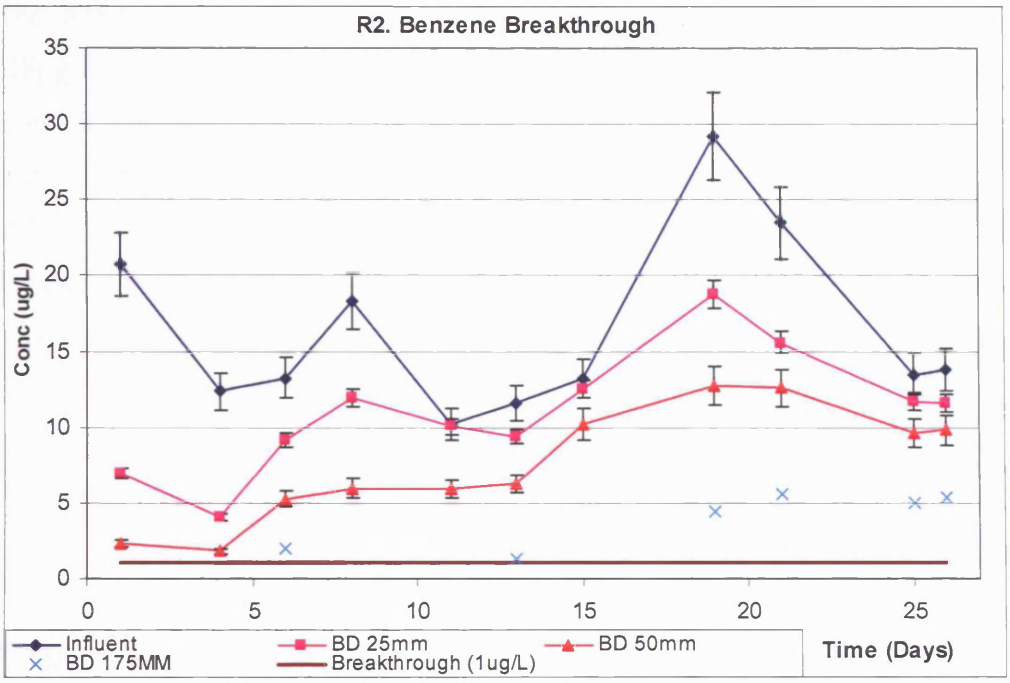


Figure 4.41. Adsorption Column Breakthrough Curve for Benzene, during Run 2.

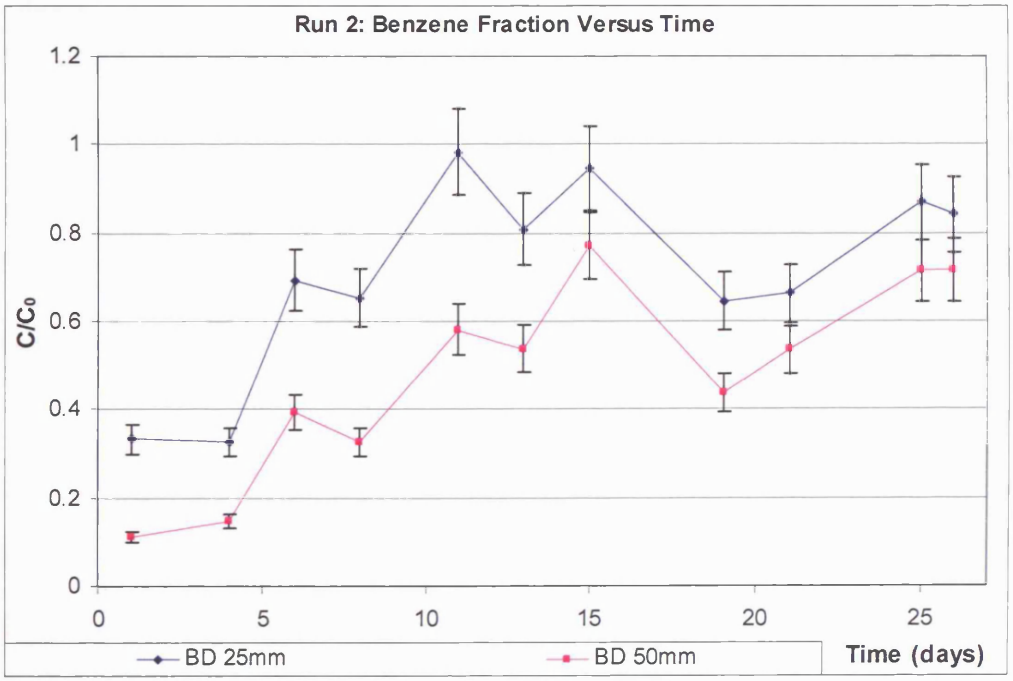


Figure 4.42. Benzene Fraction versus Time during Run 2.

Summary.

The average influent concentration of MTBE was low throughout Run 2 (18μg/L). The ARE% for bed depths 25 and 50mm was 9 and 14% respectively. Breakthrough occurred on day-1 for both bed depths. Referring to Figure 4.39 and 4.39 as the influent concentration of MTBE increased and decreased, the effluent concentration at the respective bed depths also increased and decreased. Figures 4.39 and 4.40 do not show typical adsorption breakthrough curves and was most likely caused by the fluctuating influent concentration. However, Figure 4.40 shows that the MTBE fraction did rise gradually over time. Note that the removal efficiency of F400 carbon was poor for MTBE.

The influent concentration of benzene was also low throughout Run 2 (16μg/L). The ARE% for bed depths 25 and 50mm was 25 and 52% respectively. Note that at similar influent concentrations, benzene was adsorbed more readily that MTBE. Breakthrough occurred on day-1 for both bed depths.

Referring to Figures 4.41 and 4.42 as the influent concentration increased, the concentration of benzene at both bed depths also increased. Note that Figures 4.41 and 4.42 do not show typical breakthrough curves for adsorption media.

Run 3 MTBE.

F600 Carbon.

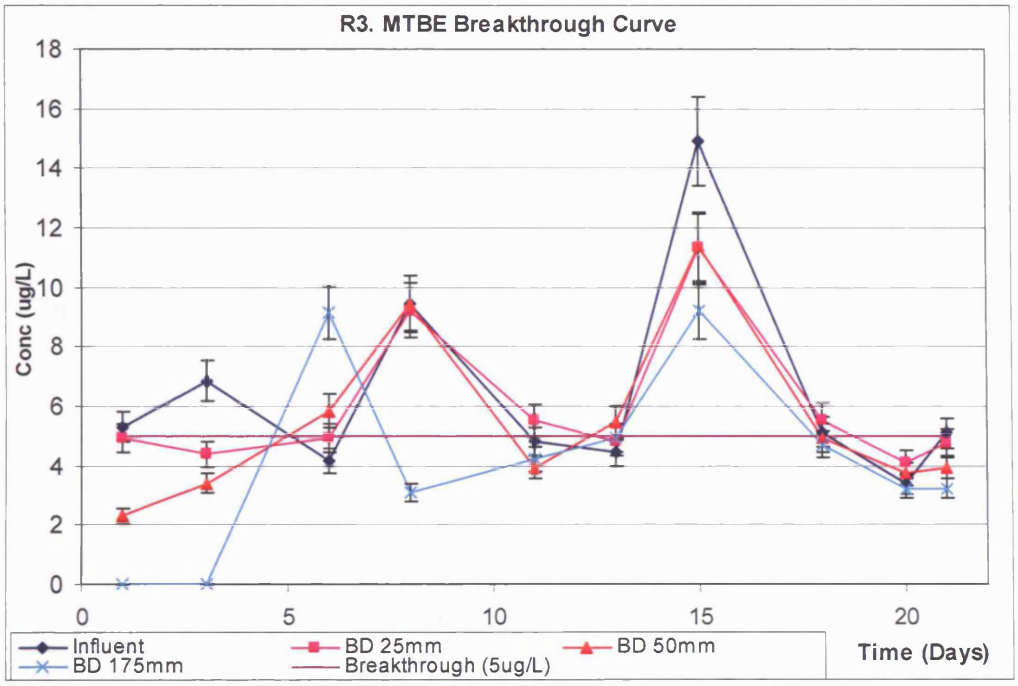


Figure 4.43. Adsorption Column Breakthrough Curve for MTBE, during Run 3.

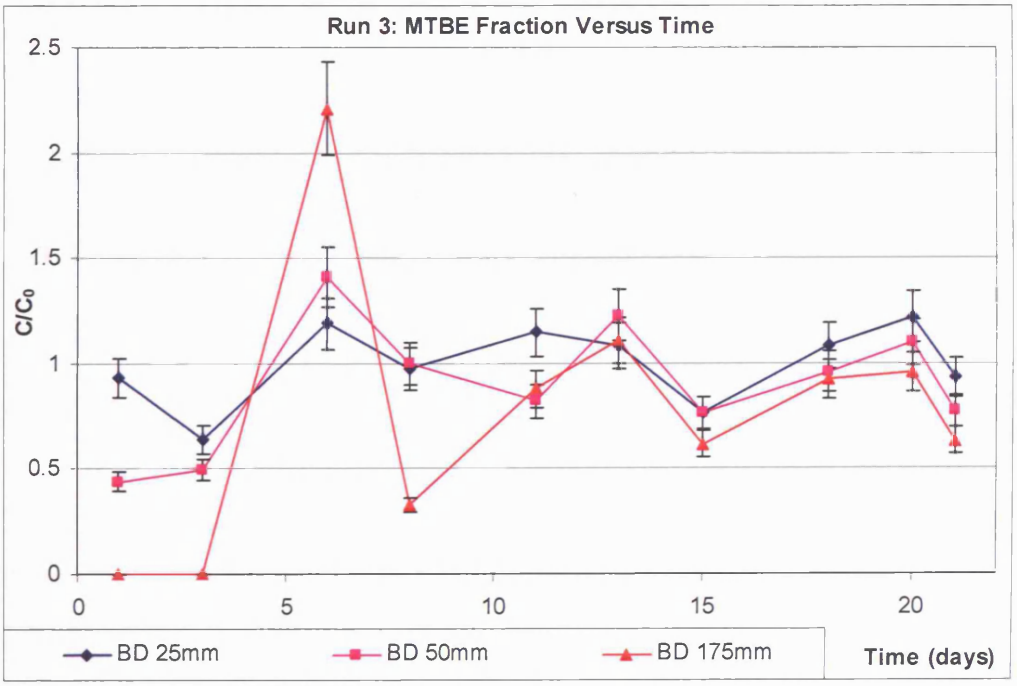


Figure 4.44. MTBE Fraction versus Time during Run 3.

Run 3 Benzene.

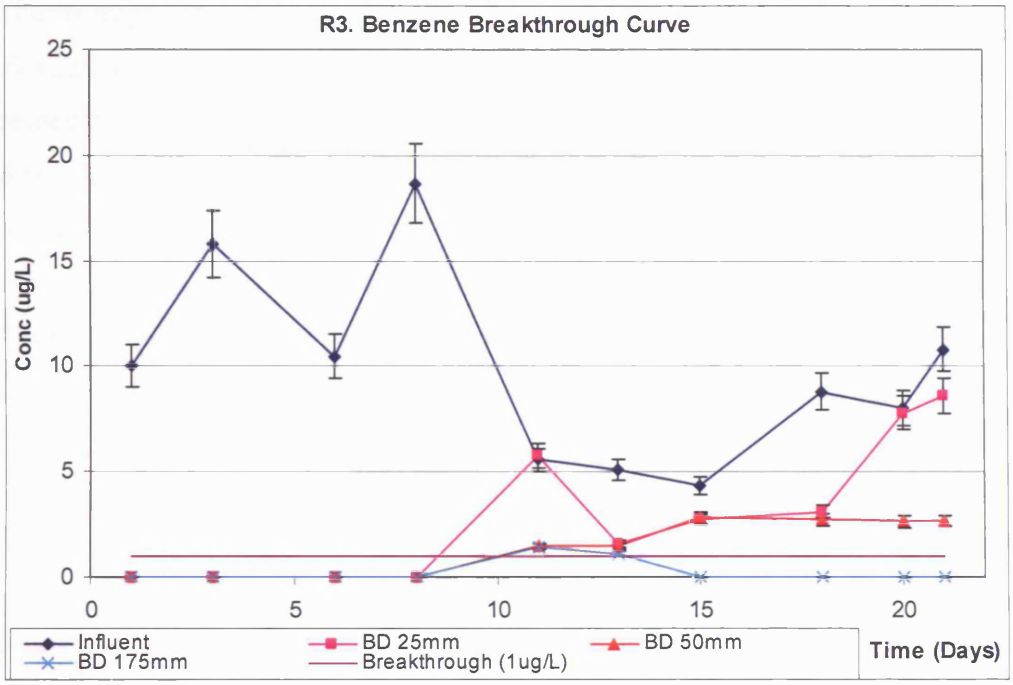


Figure 4.45. Adsorption Column Breakthrough Curve for Benzene, during Run 3.

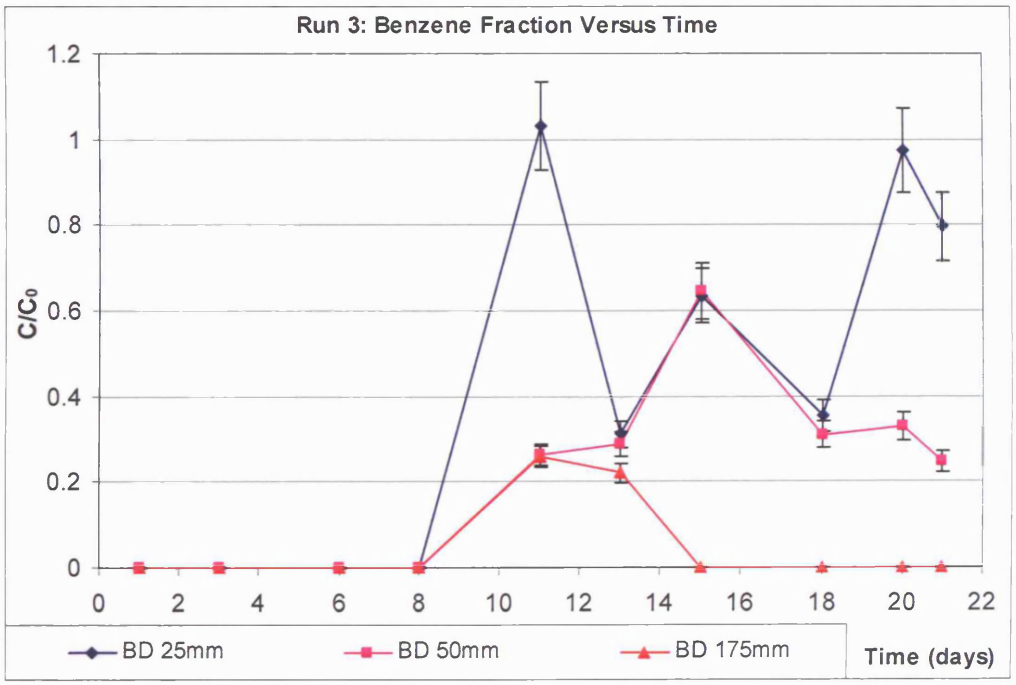


Figure 4.46. Benzene Fraction versus Time during Run 3.

Summary.

The average influent concentration of MTBE throughout Run 3 was very low (6.4μg/L). The ARE% for bed depths 25, 50 and 175mm was 15, 25 and 46% respectively. Breakthrough for bed depths 25, 50 and 175mm was on day-1, day-6 and day-6 respectively.

Figures 4.43 and 4.44 represent atypical breakthrough curves for adsorption media and were most likely caused by the variable influent concentration. Generally as the influent concentration increased, the concentration of MTBE at all bed depths also increased. Note from Figure 4.43 that as the influent concentration fluctuated above and below the 5μg/L remediation target, the concentration of MTBE in the effluent also fluctuated above and below the remediation target.

The average influent concentration of benzene throughout Run 3 was low (9.8μg/L). The ARE% for bed depths 25, 50 and 175mm was 66, 79 and 95% respectively. Breakthrough at bed depths 25, 50 and 175mm all occurred on day-11.

Due to the variable influent concentration, Figures 4.45 and 4.46 do not represent typical adsorption breakthrough curves. Note that apart from day-11, the remediation target for benzene was achieved for bed depth 175mm.

Note that at similar influent concentrations, benzene was more amenable to adsorption than MTBE.

Run 4 MTBE.

F600 Carbon.

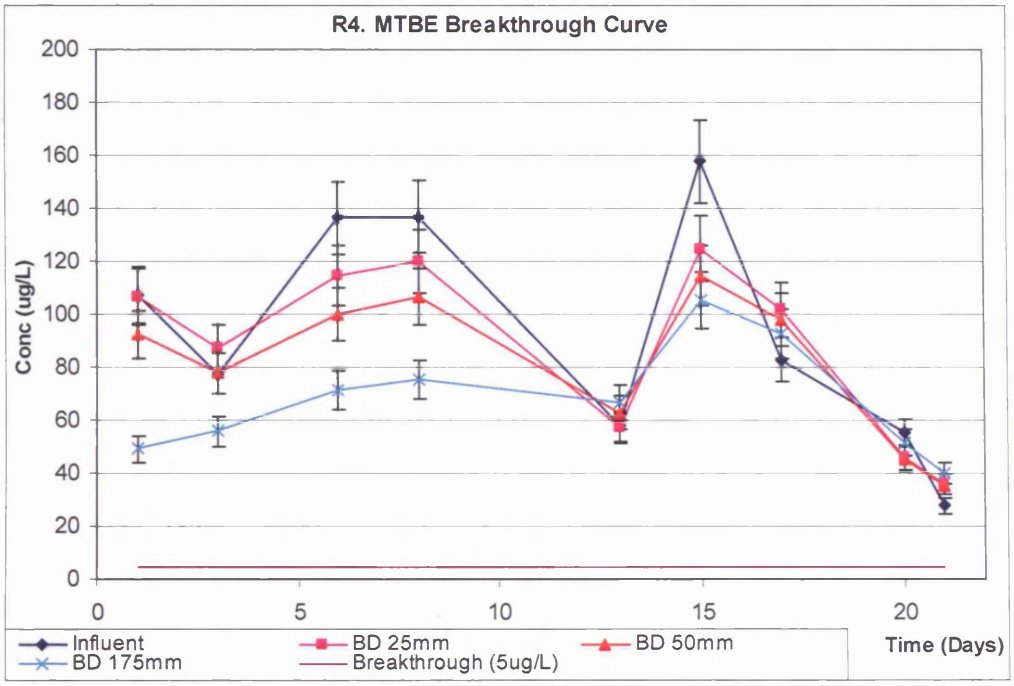


Figure 4.47. Adsorption Column Breakthrough Curve for MTBE, during Run 4.

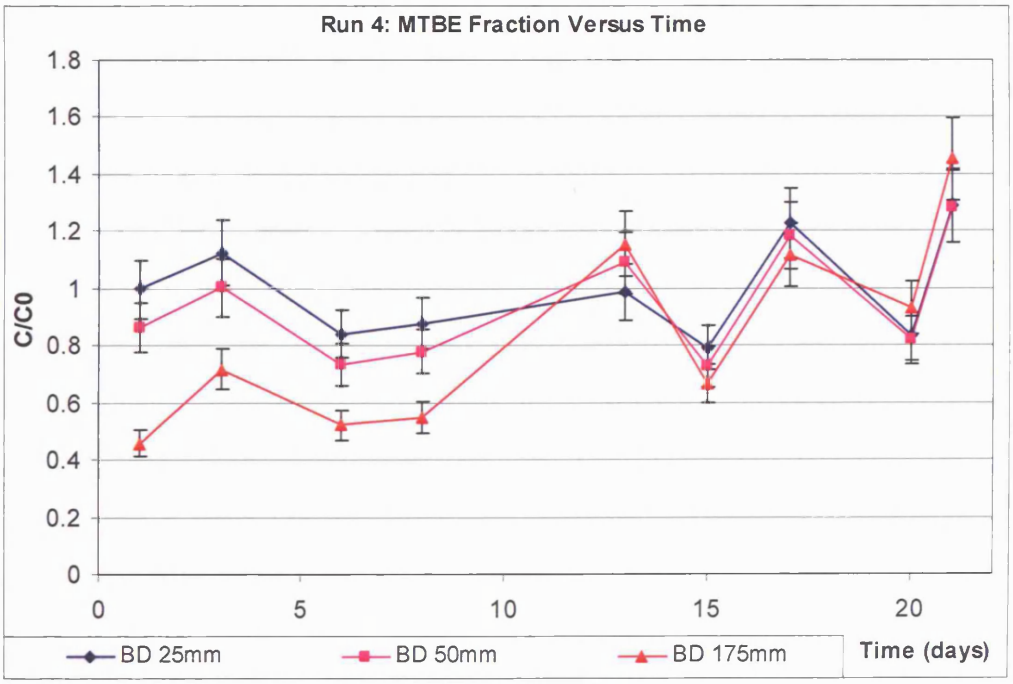


Figure 4.48. MTBE Fraction versus Time during Run 4.

Run 4 Benzene.

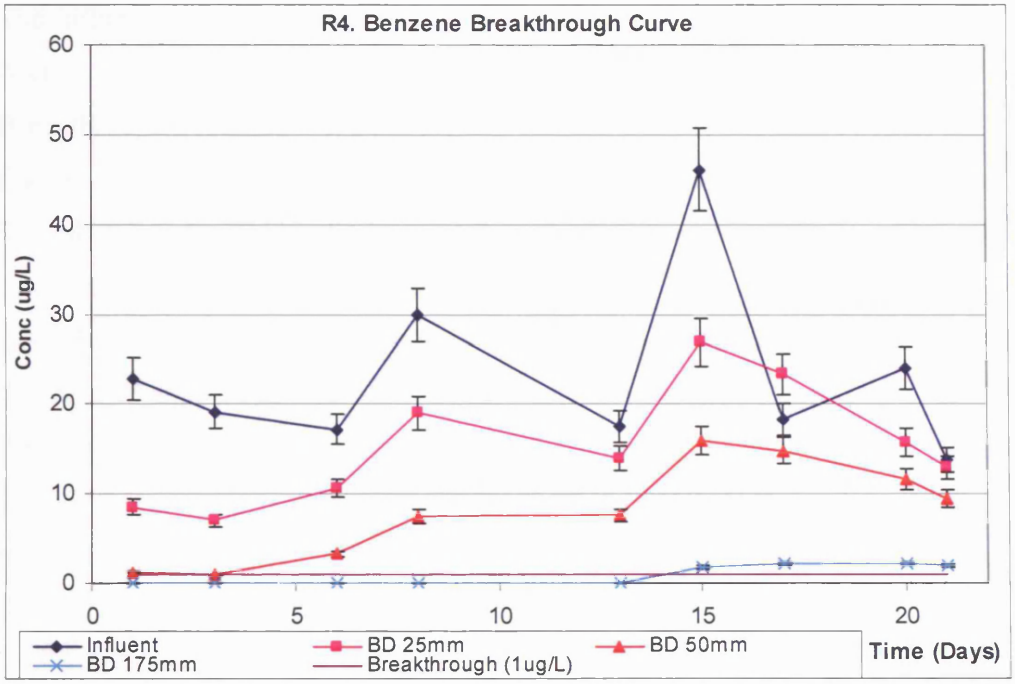


Figure 4.49. Adsorption Column Breakthrough Curve for Benzene, during Run 4.

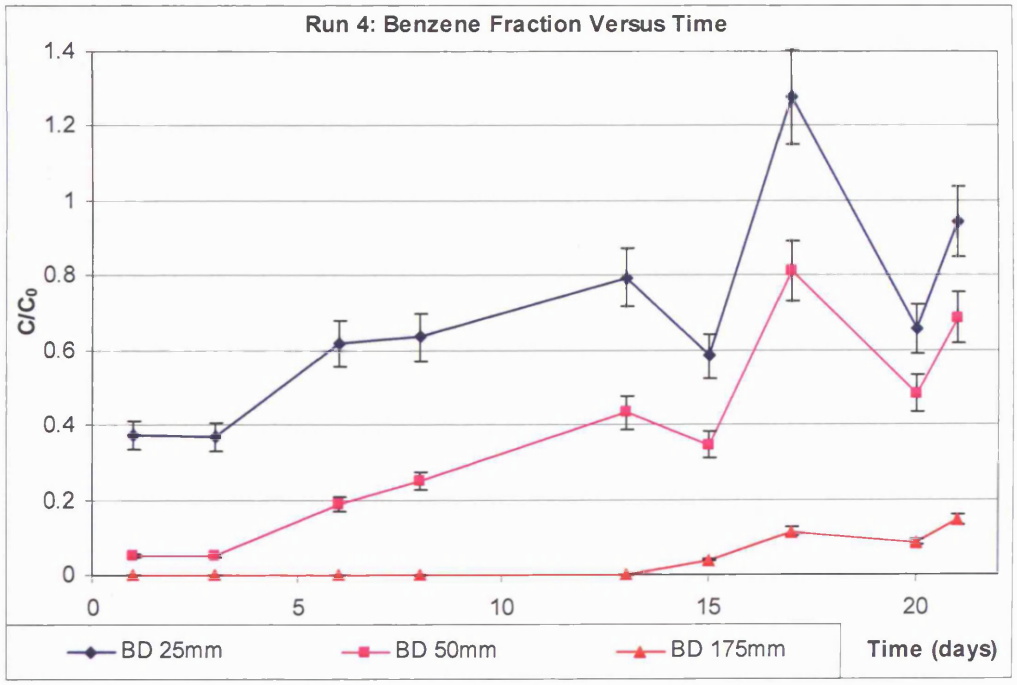


Figure 4.50. Benzene Fraction versus Time during Run 4.

Summary.

The influent concentration of MTBE was high throughout Run 4 (93µg/L). The ARE% for bed depths 25, 50 and 175mm was 11, 22 and 45% respectively. Breakthrough of MTBE occurred on day-1 for all bed depths.

Figures 4.47 and 4.48 do not represent typical adsorption breakthrough curves for MTBE. As the influent concentration increases and decreases, the concentration of MTBE in all bed depths also increases and decreases. Note that towards the end of the test, the influent concentration decreases.

Figure 4.48 shows reasonable correlation between the fraction of MTBE passing through the F600 carbon at all bed depths. The overall trend for the MTBE fraction is to increase over time. Figure 4.48 shows that desorption occurs for most of the test, suggesting that equilibrium has been achieved.

The average influent concentration of benzene throughout Run 4 was 23µg/L. The ARE% for bed depths 25, 50 and 175mm was 31, 63 and 96% respectively. Breakthrough for bed depths 25, 50 and 175mm was on day-1, day-1 and day-15 respectively.

Referring to Figure 4.49 and 4.50, as the influent concentration of benzene increases and decreases, the concentration at all bed depths also fluctuates. The general trend throughout Figures 4.49 and 4.50 is for the benzene fraction to increase over time. This is more typical of a generalised adsorption curve.

Run 5 MTBE.

F400.

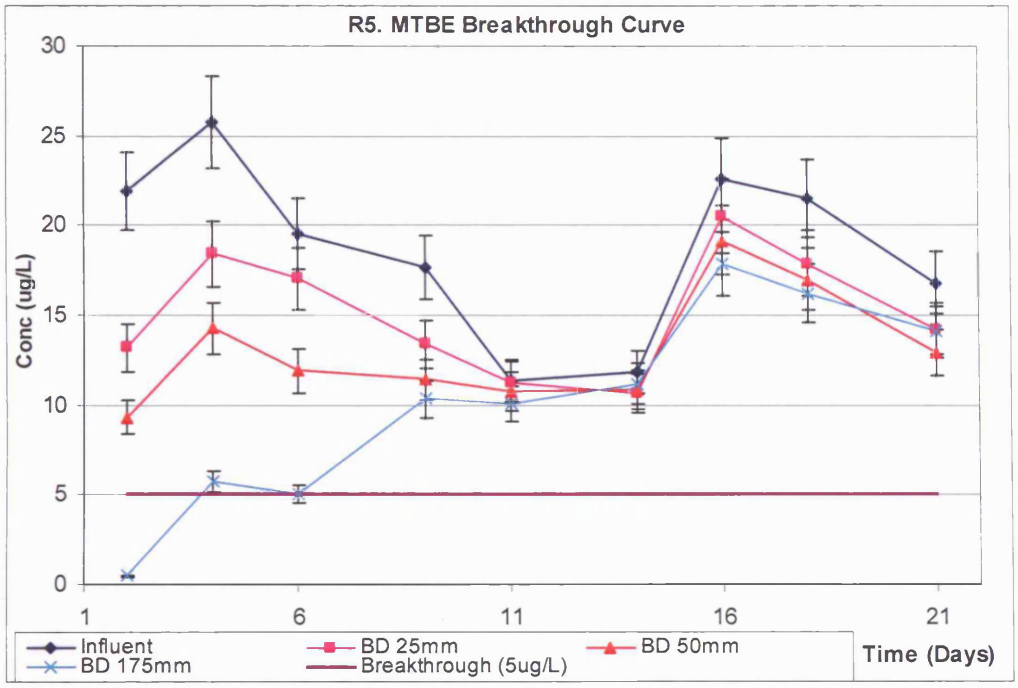


Figure 4.51. Adsorption Column Breakthrough Curve for MTBE, during Run 5.

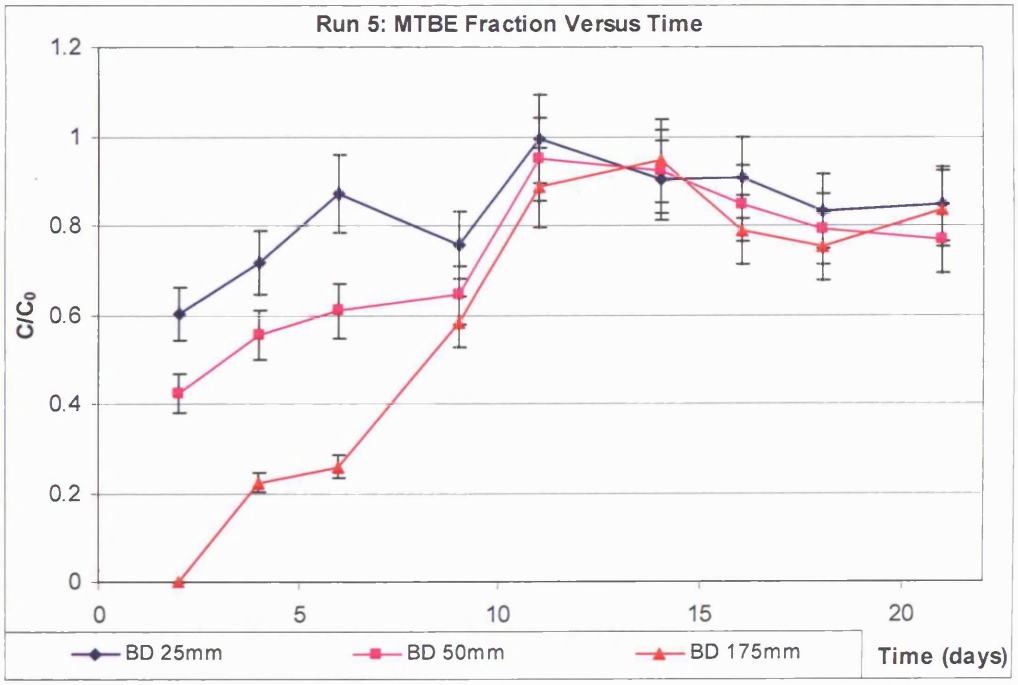


Figure 4.52. MTBE Fraction versus Time during Run 5.

Run 5 Benzene.

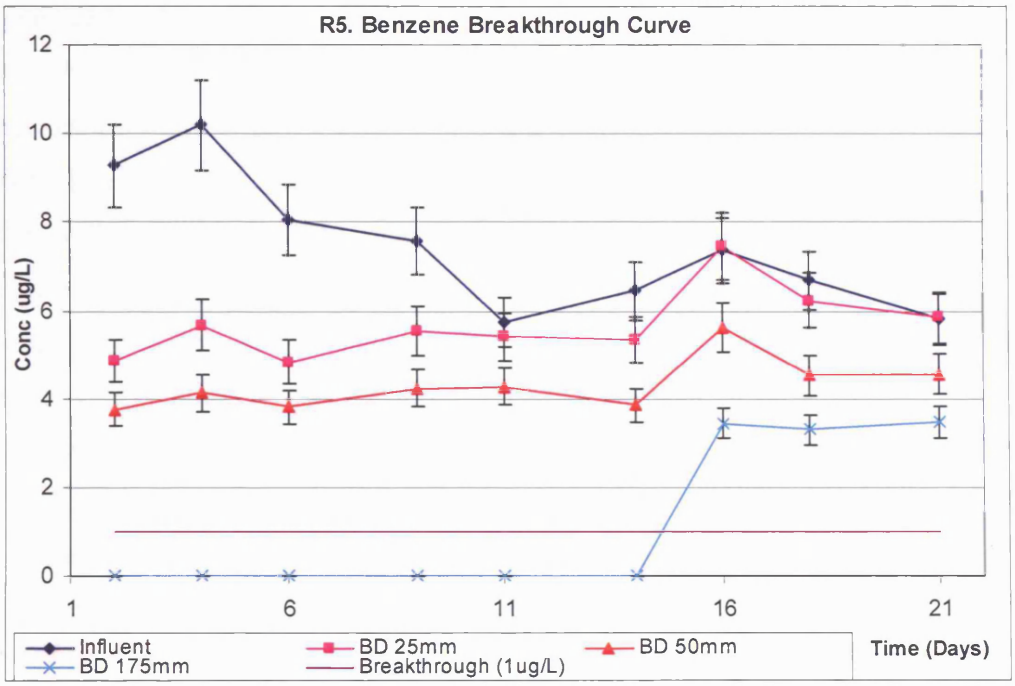


Figure 4.53. Adsorption Column Breakthrough Curve for Benzene, during Run 5.

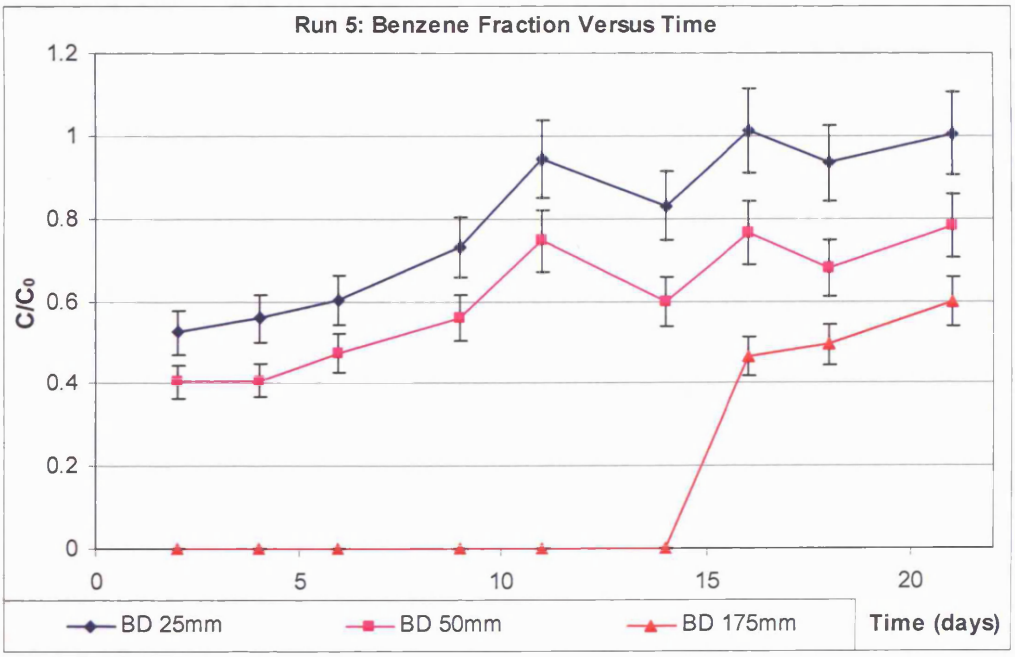


Figure 4.54. Benzene Fraction versus Time during Run 5.

Summary.

The average influent concentration of MTBE throughout Run 5 was 19μg/L. The ARE% for bed depths 17, 28 and 41% respectively. Breakthrough of MTBE occurred on day-2, day-2 and day-4 respectively (although note that a test was not taken on day-1).

Generally as the influent concentration of MTBE fluctuates, the effluent concentration of MTBE in all bed depths also fluctuates. Referring to Figure 4.52, the fraction of MTBE passing through the carbon generally increases over time. This is more typical of an adsorption breakthrough curve.

The average influent concentration of benzene throughout Run 5 was low (7.5μg/L). The ARE% for bed depths 25, 50 and 175mm was 27, 40 and 83% respectively. Breakthrough for benzene occurred on day-2, day-2 and day-16 for bed depths 25, 50 and 175mm respectively (note that a test was not taken on day-1).

Referring to Figure 4.54, the general trend for the benzene fraction in the effluent is to increase over time. This is more typical of an adsorption breakthrough curve. Note that towards the end of the test, the fraction of benzene passing through the carbon approaches one, suggesting that the system has reached equilibrium.

Run 6 MTBE.

F400 Carbon.

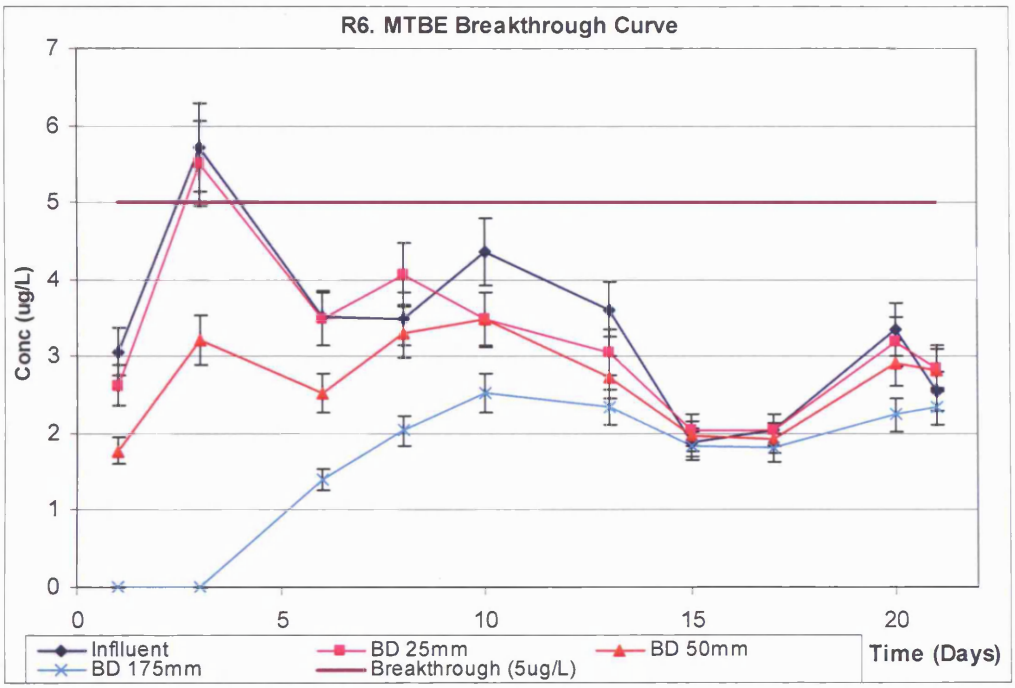


Figure 4.55. Adsorption Column Breakthrough Curve for MTBE, during Run 6.

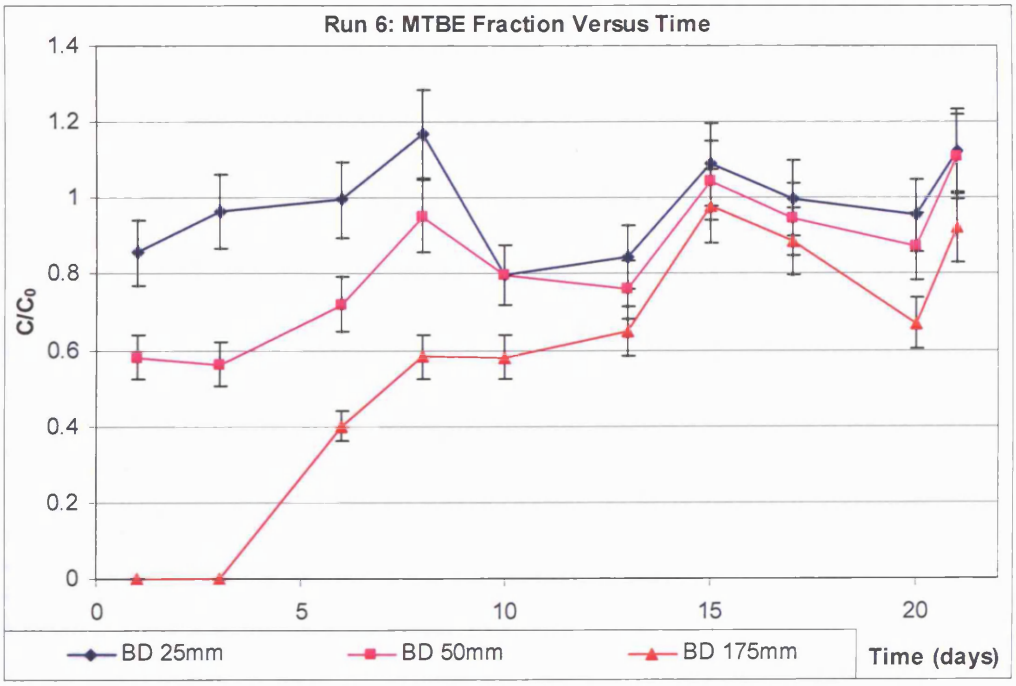


Figure 4.56. MTBE Fraction versus Time during Run 6.

Run 6 Benzene.

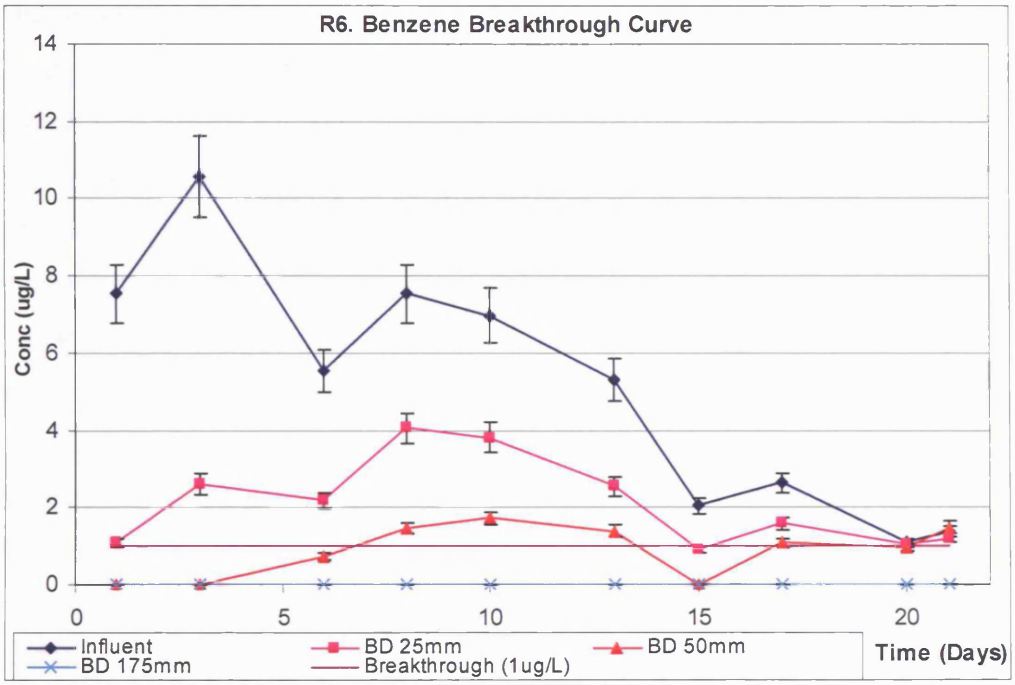


Figure 4.57. Adsorption Column Breakthrough Curve for Benzene, during Run 6.

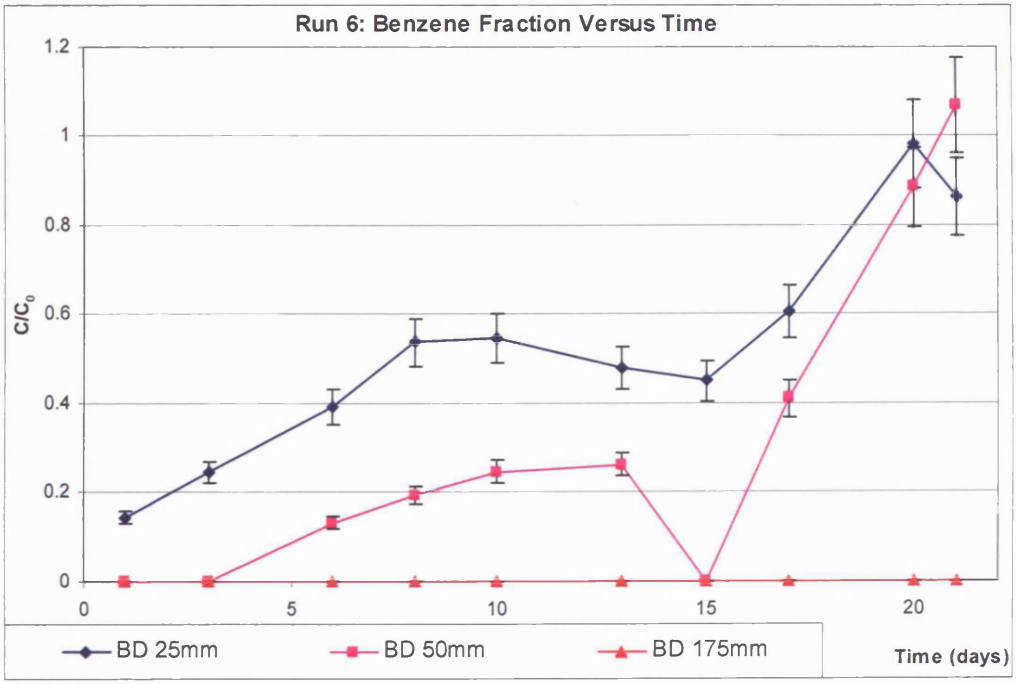


Figure 4.58. Benzene Fraction versus Time during Run 6.

Summary.

The average influent concentration of MTBE throughout Run 6 was very low (3.4µg/L). The ARE% for bed depths 25, 50 and 175mm was 11, 23 and 43% respectively. Breakthrough occurred on day-3 for bed depth 25mm. The concentration of benzene in bed depths 50 and 175mm did not exceed the 5µg/L remediation target.

Referring to Figure 4.55 it can be noted that the influent concentration remained below the remediation target for the duration of the test, apart from on day-3. The general trend throughout the experimental phase was that as the influent concentration increased, the effluent concentration increased. For this reason, breakthrough occurred on day-3 for bed depth 25mm.

Referring to Figure 4.56, it can be seen that the curve for the fraction of MTBE passing through the carbon represents a more typical adsorption curve.

The average influent concentration of benzene throughout Run 6 was very low (5.1µg/L). The ARE% for bed depths 25, 50 and 175mm was 48, 77 and 100% respectively. Breakthrough occurred on day-1 and day-8 for bed depths 25 and 50mm. The concentration of benzene in the effluent of bed depth 175mm did not exceed the remediation target at any point throughout the test.

Referring to Figures 4.57 and 4.58, as the influent concentration increased and decreased, the concentration of benzene in the effluent also varied. Figure 4.58 represents a more typical adsorption breakthrough curve, although the general increase may have been caused by a fall in the influent concentration towards the end of the test.

Run 7 MTBE.

F600 Carbon.

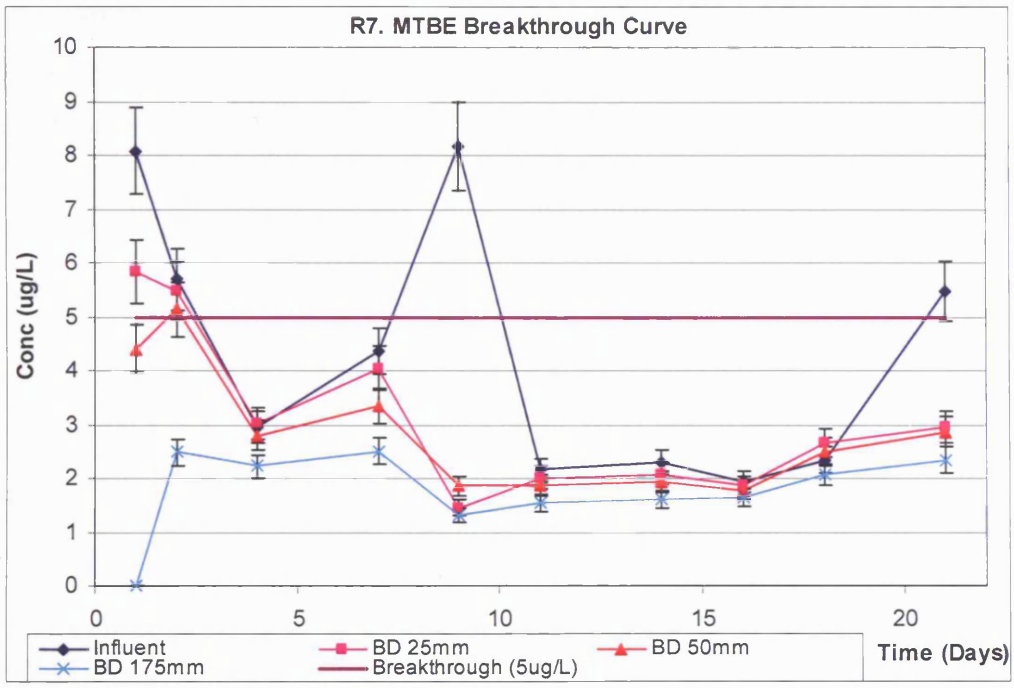


Figure 4.59. Adsorption Column Breakthrough Curve for MTBE, during Run 7.

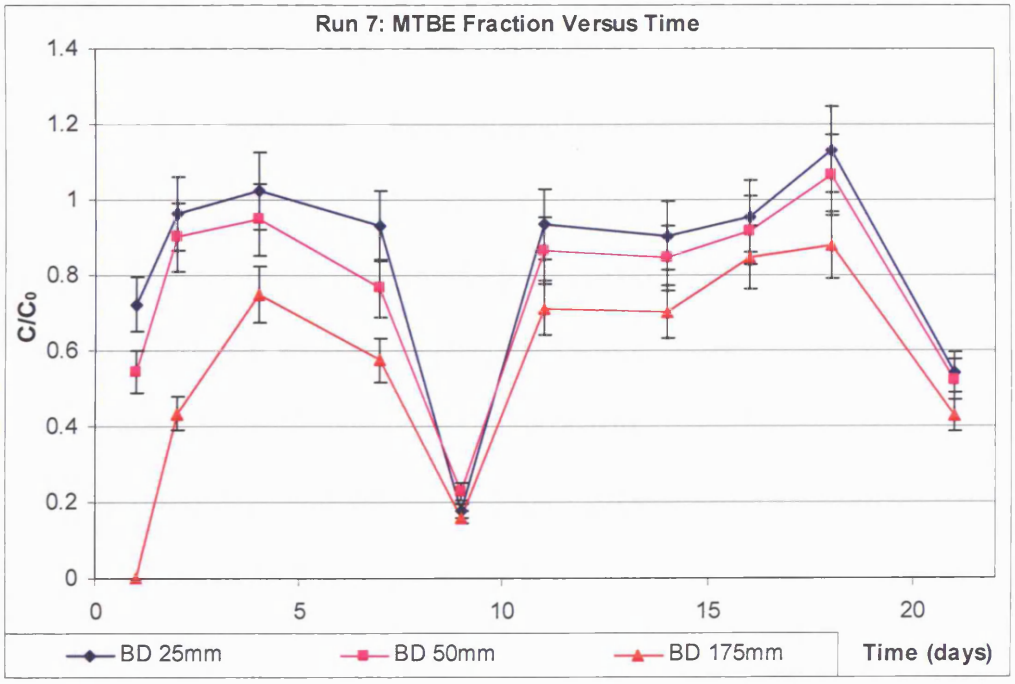


Figure 4.60. MTBE Fraction versus Time during Run 7.

Summary.

The influent concentration of MTBE throughout Run 7 was very low (4.4μg/L). The ARE% for bed depths 25, 50 and 175mm was 21, 27 and 44% respectively. Breakthrough for bed depth 25mm was on day-1, whilst breakthrough for bed depth 50mm was on day-2. Bed depth 175mm achieved the remedial target of 5μg/L for the duration of the test. Note from Figure 4.59 that the influent concentration was very erratic and fell below the 5μg/L remediation target for most of the test. The influent concentration was above the remediation target at the beginning of the test, which corresponded to breakthrough for bed depths 25 and 50mm. Once the influent concentration fell below 5μg/L, the effluent concentrations also fell below the target concentration.

Referring to Figure 4.60 it can be noted that as the influent concentration sharply rose on day-9, the MTBE fraction passing through the carbon fell. This suggests that the F600 carbon still had capacity to adsorb. However, the efficiency of adsorption throughout the remainder of the test was poor. Since adsorption is an equilibrium process, adsorption of solutes can increase at higher influent concentrations.

Run 8 MTBE.

F600 Carbon.

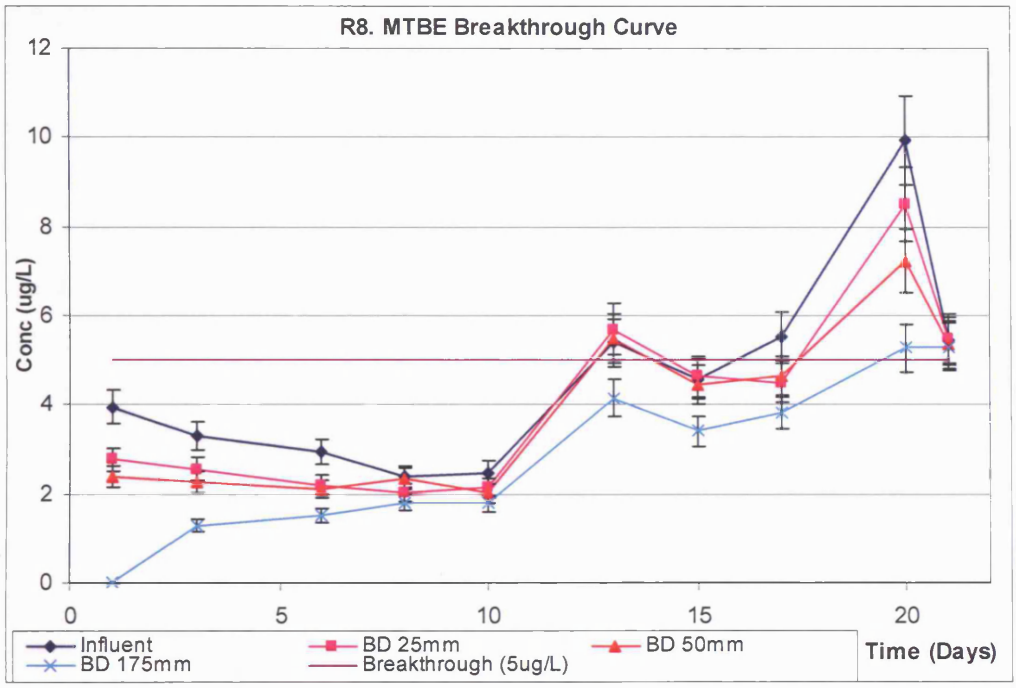


Figure 4.61. Adsorption Column Breakthrough Curve for MTBE, during Run 8.

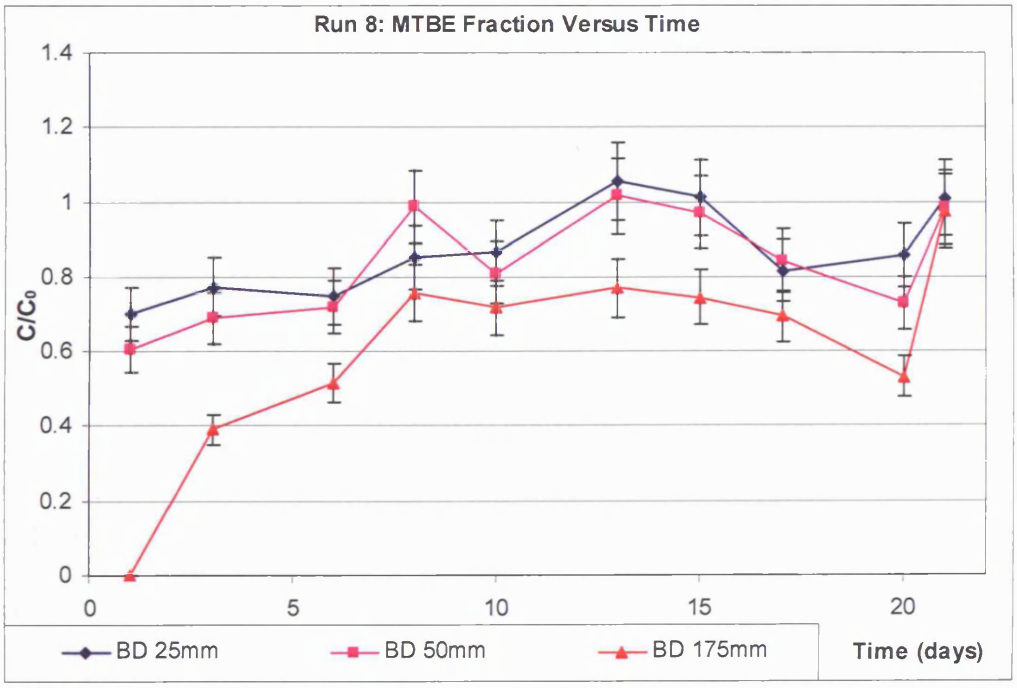


Figure 4.62. MTBE Fraction versus Time during Run 8.

Summary.

The average influent concentration of MTBE throughout Run 8 was very low (4.6µg/L). The ARE% for bed depths 25, 50 and 175mm was 20, 19 and 37% respectively. Breakthrough for bed depths 25, 50 and 175mm occurred on day-13, day-13 and day-20 respectively.

Referring to Figure 4.61 it can be noted that the influent concentration remained below the remediation target for most of the test. Only when the influent concentration rose above 5µg/L did the effluent concentration breach the remediation target.

Due to the fluctuating influent concentration, Figures 4.61 and 4.62 did not represent typical adsorption breakthrough curves.

Run 8 – Repeat MTBE.

F600 Carbon.

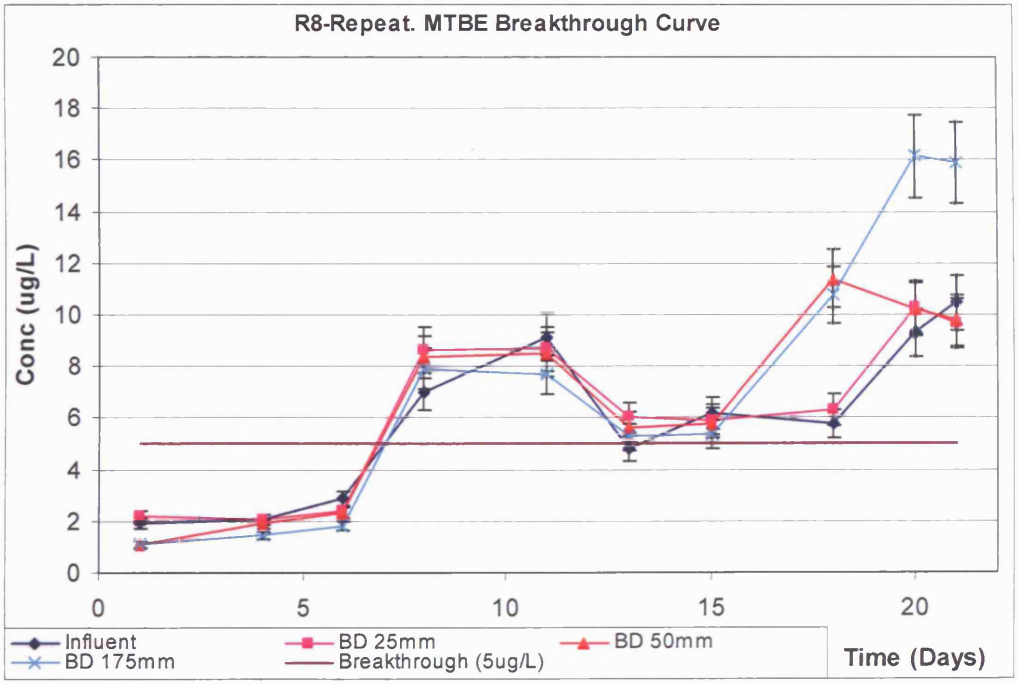


Figure 4.63. Adsorption Column Breakthrough Curve for MTBE, during Run 8 Repeat.

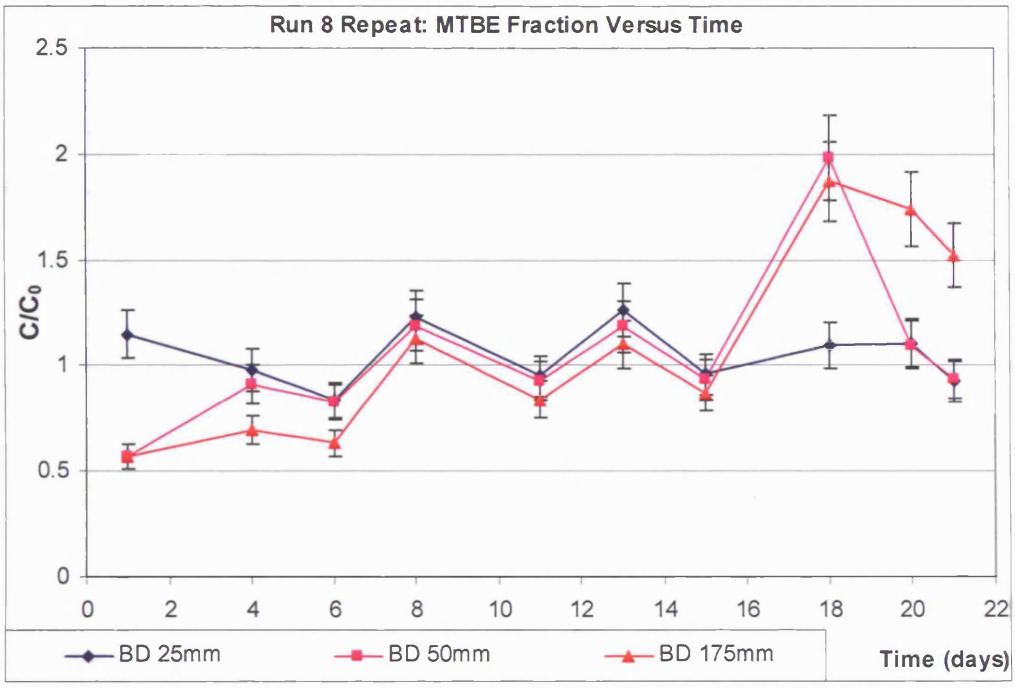


Figure 4.64. MTBE Fraction versus Time during Run 8 Repeat.

Run 8 Repeat Benzene.

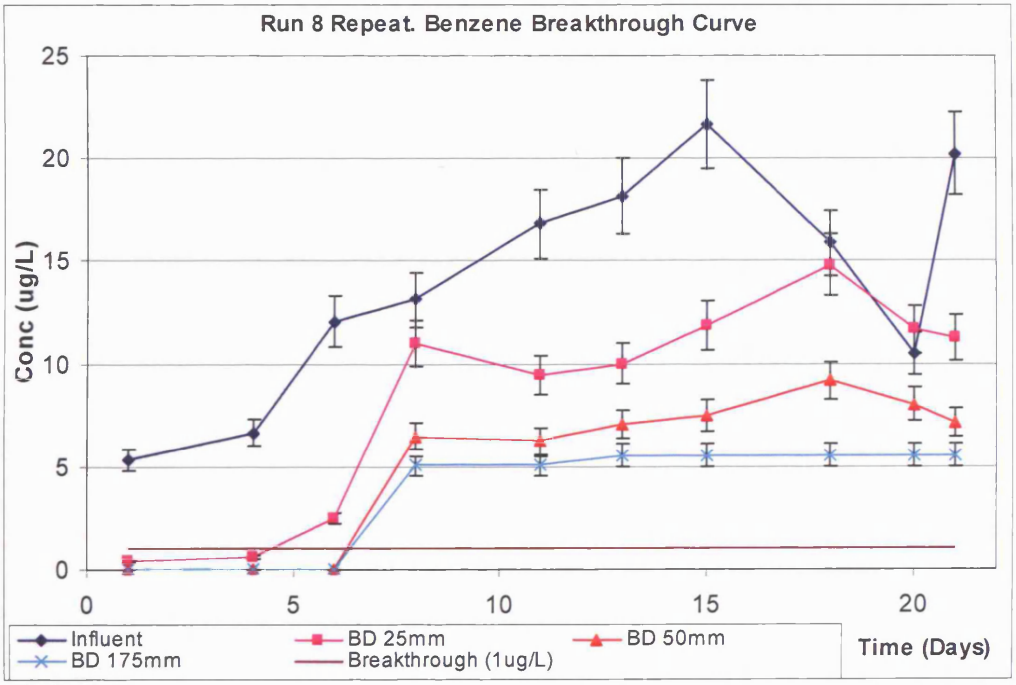


Figure 4.65. Adsorption Column Breakthrough Curve for Benzene, during Run 8 Repeat.

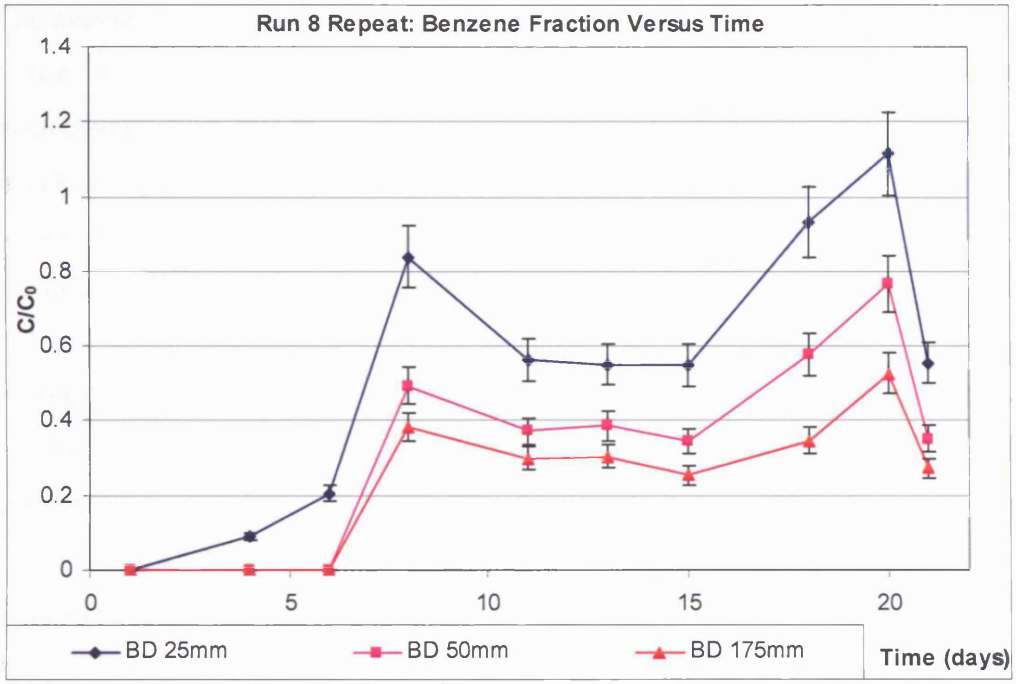


Figure 4.66. Benzene Fraction versus Time during Run 8 Repeat.

Summary.

The average influent concentration of MTBE throughout Run 8 Repeat was low (6.4µg/L). The ARE% for bed depths 25, 50 and 175mm was 7, 24 and 29% respectively. Breakthrough for bed depths 25, 50 and 175mm occurred on day-8, day-8 and day-8 respectively. As with Run 8, the influent concentration of MTBE rose steadily throughout Run 8 Repeat. This transposed into similar breakthrough curves (presented in Figures 4.63 and 4.64). Note from Figure 4.63 that breakthrough only occurred once the influent concentration rose above 5µg/L on day-8.

As with the remainder of Runs 1 – 8, as the influent concentration increased and decreased, the effluent concentration of MTBE at all bed depths also increased and decreased.

Note from Figure 4.64 that desorption of MTBE occurred throughout the test. Desorption may have occurred due to the low influent concentration experienced throughout the test. This may have lowered the adsorption equilibrium of the system.

The average influent concentration of benzene throughout Run 8 Repeat was low (14μg/L). The ARE% for bed depths 25, 50 and 175mm 45, 67 and 76% respectively. Note that this was significantly greater than the ARE% for MTBE. Breakthrough for bed depths 25, 50 and 175mm was on day-6, day-8 and day-8 respectively. However, breakthrough would have been dictated by the fact that the influent concentration of benzene steadily rose throughout the duration of the test.

Figures 4.65 and 4.66 represent typical breakthrough curves. However, the shape of the curve was most likely affected by the gradual rise in the influent concentration.

Adsorption Column Summary.

In order to summarise the adsorption column results, table 4.16 – 4.17 present the overall results from Run 1 – Run 8 Repeat including;

- Average influent concentration (μg/L)
- Average effluent concentration (μg/L)
- Average removal efficiency (ARE%)
- Time to component breakthrough (d)
- Bed volumes to component breakthrough (L)
- Mass removed until component breakthrough (g)
- Capacity of carbon at breakthrough (mg/g)
- Total mass throughout entire test (g)
- Total capacity of carbon throughout entire test (mg/g)

Results are presented for all three bed depths where BD = Bed depth and NBT= No breakthrough.

	RUN 1 – F400						RUN 2 – F400					
	MTBE			BENZENE			MTBE			BENZENE		
	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm
Av. Influent Conc (ug/L)		89			13			18			16	
Av. Effluent (ug/L)	80	76	NDA	4.9	2.7	NDA	17	16	NDA	11	7.5	NDA
ARE%	14	24	NDA	62	82	NDA	9	14	NDA	29	52	NDA
BT (Days)	1	1	NDA	4	6	NDA	1	1	NDA	1	1	NDA
BT (Bed Volumes)	7714	3847	NDA	30857	23084	NDA	7714	3847	NDA	7714	3847	NDA
Mass adsorbed until BT (g)	0.0075	0.0498	NDA	0.0592	0.0883	NDA	0.0045	0.0091	NDA	0.0213	0.0283	NDA
Capacity until BT (mg/g)	0.09			0.69			0.05			0.25		
Total Mass Adsorbed (g)	0.2971	0.4104	NDA	0.2343	0.3027	NDA	0.0522	0.0881	NDA	0.2064	0.3524	NDA
Total Capacity (mg/g)	3.45			2.72			0.61			2.40		
	RUN 3 – F600						RUN 4 – F600					
	MTBE			BENZENE			MTBE			BENZENE		
	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm
Av. Influent Conc (ug/L)		6.4			9.8			93			23	
Av. Effluent (ug/L)	6.0	5.4	4.2	3.0	1.4	<1	88	81	68	15	8.0	<1
ARE%	15	25	46	66	79	95	11	22	45	31	63	96
BT (Days)	1	6	6	11	11	11	1	1	1	1	1	15
BT (Bed Volumes)	7714	23048	6622	84857	42321	12140	7714	3847	1104	7714	3847	16554
Mass adsorbed until BT (g)	0.0006	0.0182	0.0305	0.2031	0.2127	0.2129	0.0015	0.0419	0.0892	0.0219	0.0329	0.5264
Capacity until BT (mg/g)	0.01			1.64			0.01			0.18		
Total Mass Adsorbed (g)	0.0172	0.0319	0.0734	0.2430	0.2769	0.3073	0.1852	0.4142	0.9034	0.2543	0.5054	0.7287
Total Capacity (mg/g)	0.14			1.96			1.49			2.05		

Table 4.17. Adsorption Column Summary Table for Runs 1 – 4.

	RUN 5 – F400						RUN 6 – F400					
	MTBE			BENZENE			MTBE			BENZENE		
	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm
Av. Influent Conc (ug/L)		19			7.5			3.4			5.1	
Av. Effluent (ug/L)	15	13	10	5.7	4.3	1.1	3.2	2.7	1.7	2.1	<1	<1
ARE%	17	28	41	27	40	83	11	23	43	48	77	100
BT (Days)	2	2	4	2	2	16	NBT	NBT	NBT	1	8	NBT
BT (Bed Volumes)	15429	7695	4415	15429	7695	17658	NBT	NBT	NBT	7714	30779	NBT
Mass adsorbed until BT (g)	0.0272	0.0384	0.1304	0.0133	0.0166	0.1849	NBT	NBT	NBT	0.0098	0.0948	NBT
Capacity until BT (mg/g)	0.32			0.15				0.09			0.11	
Total Mass Adsorbed (g)	0.1254	0.1982	0.3092	0.0606	0.1046	0.2091	0.0074	0.0266	0.0606	0.1071	0.1536	0.1750
Total Capacity (mg/g)	1.46			0.70				0.09			1.25	
	RUN 7 – F600						RUN 8 – F600					
	MTBE			BENZENE			MTBE			BENZENE		
	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm	25mm	50mm	175mm
Av. Influent Conc (ug/L)		4.4						4.6				
Av. Effluent (ug/L)	3.1	2.9	1.8				4.1	3.8	2.8			
ARE%	21	27	44				20	19	37			
BT (Days)	1	2	NBT				13	13	20			
BT (Bed Volumes)	7714	7695	NBT				100286	50015	22073			
Mass adsorbed until BT (g)	0.0035	0.0088	NBT				0.0109	0.0133	0.0544			
Capacity until BT (mg/g)	0.03						0.09					
Total Mass Adsorbed (g)	0.0326	0.0413	0.0703				0.0184	0.0249	0.0579			
Total Capacity (mg/g)	0.26						0.15					

Table 4.18. Adsorption Column Summary Table for Runs 5 – 8.

	RUN 8 REPEAT (TAGUCH VERIFICATION TEST)					
	MTBE			BENZENE		
	25mm	50mm	175mm	25mm	50mm	175mm
Av. Influent Conc (ug/L)		6.4			14	
Av. Effluent (ug/L)	5.7	5.0	5.2	8.3	5.2	3.8
ARE%	7	24	29	45	67	76
BT (Days)	8	8	8	6	8	8
BT (Bed Volumes)	61714	30778	8829	46285	30778	8829
Mass adsorbed until BT (g)	0.0051	0.0064	0.0109	0.0593	0.0910	0.0933
Capacity until BT (mg/g)	0.04			0.48		
Total Mass Adsorbed (g)	0.0195	0.0298	0.0333	0.1813	0.2769	0.3201
Total Capacity (mg/g)	0.16			1.47		

Table 4.19. Adsorption Column Summary Table for Run 8 Repeat.

Throughout Chapter 4.3 it can be noted that the adsorption column results were adversely affected by the variable influent concentration. Throughout Figures 4.35 – 4.66, generally as the influent concentration increased and decreased, the concentration of MTBE and benzene in the effluent increased and decreased.

Although breakthrough data was generated throughout the experimental phase, caution was exercised when interpreting the data due to the variable influent concentration. For example referring to Run 8, MTBE broke through the 5µg/L remediation target on day-13, day-13 and day-20 for bed depths 25, 50 and 175mm respectively. However referring to Figure 4.61, breakthrough only occurred as the influent concentration rose above the 5µg/L remediation target towards the end of the test.

The raw influent and effluent data was reinterpreted in order to take into account the variable influent concentration. This was achieved by calculating the fraction of MTBE and benzene passing through the carbon and was plotted against time. As the fraction approaches 1, system equilibrium for the given influent concentration has occurred. Referring to the figures throughout Chapter 4.3, it can be noted that even with this additional calculation, typical adsorption breakthrough curves were generally not observed. However some experiments (for example Run 5) did present characteristic breakthrough trends.

It can be noted throughout experimental period that desorption of the given adsorbate sometime occurred (for example Run 8 Repeat). It is possible that at low influent concentrations, equilibrium is achieved between the influent and

effluent, hence leading to desorption of the adsorbate back into solution. As previously detailed, desorption is taken into account within the capacity calculations.

Referring to Run 7 (Figures 4.59 and 4.60) the fraction of MTBE is close to 1 for most of the test, suggesting that equilibrium has been achieved. However, when the influent concentration increases sharply on day-9, the equilibrium shifts and the fraction of MTBE passing the carbon dramatically reduces.

Separation through adsorption occurs because differences in molecular weight, shape and polarity cause a greater affinity of some compounds for the GAC than others. Hydrophilic and hence soluble compounds such as MTBE are known to be less amenable to adsorption onto carbon substrates than compounds such as benzene, due to the polar nature of the compound. This trend is seen throughout the experimental phase of the study when the ARE% and capacity data is generally greater for benzene than it is for MTBE. For example referring to Run 3, the influent concentration of MTBE and benzene were similar, yet the ARE% is much greater for benzene than it is for MTBE.

Breakthrough of MTBE generally occurs before that of benzene, although as suggested previously breakthrough data must be viewed with caution.

Referring to Runs 2, 3 and 6, the influent concentrations of MTBE and benzene are similar. However it can be noted that ARE% and adsorptive capacity data is more favourable for benzene. This suggests that competitive adsorption is taking place in the MTBE-benzene system. Competitive adsorption between benzene and MTBE (and in some cases the displacement of MTBE by BTEX compounds) is documented in literature (e.g. Sorial *et al*, 1993). Note that competitive adsorption will not only occur between MTBE and benzene, but between the remainder of the TEX compounds also. TEX compounds are also known to be more amenable to adsorption than MTBE.

In the case of mixtures, competitive displacement of previously adsorbed compounds (such as MTBE) from those compounds more amenable to adsorption (e.g. benzene) can sometimes occur. In these cases, the effluent concentration of MTBE may be greater than the influent concentration.

In addition to the adsorbates included in the study, literature suggested that competitive adsorption can also occur between BOM and NOM. BOM and NOM can impact the removal of specific organics such as MTBE and BTEX by

reducing the number of adsorption sites, blockage of the pores and the irreversible adsorption to GAC adsorption sites (Shih *et al*, 2003). This can cause reduction in the adsorptive capacity of the carbon. Note that NOM and BOM are generally low in natural groundwaters.

Data from Thames Water (Appendix F) suggests that the TOC for the laboratory water is 3mg/L. It is therefore possible that the presence of TOC may contribute to a reduction in the overall adsorptive capacity of the carbon within the experimental phase.

4.4. Taguchi Method Results.

Within this section experiments are identified by their Taguchi experimental numbers, rather than the chronological experimental order used so far throughout Chapter 4. Refer to Table 3.13 (Section 3.2.8 of Chapter 3) for equivalent test numbers.

The results of the Taguchi Method are detailed in this section. As discussed previously, the Taguchi analysis takes into account both the air-stripping and adsorption technologies combined.

Experimental limitations due to selective biodegradation of benzene occurred throughout Taguchi Runs 2 and 5. This was caused by the excessive sample storage period experienced throughout the tests. With respect to Taguchi Runs 2 and 5, experimental data was limited to MTBE only hence a full set of results was not available for benzene. This meant that the Taguchi array could not be completed for benzene. MTBE was used to complete the Taguchi analysis using the available data, where breakthrough was defined as the time to MTBE breakthrough at the required bed depth, to concentrations of 5μg/L.

As discussed in previous sections, problems were experienced throughout all of the tests with regards to controlling the influent concentration. Since the time to MTBE breakthrough would be affected by the influent concentration, Taguchi results based upon time to breakthrough may not be accurate. In order to express the Taguchi breakthrough data independently from the influent concentration, the results were converted into mass removed until breakthrough as a fraction of the total influent mass (FMR). The FMR calculation was similar to those detailed in section 4.3, but was applied to the combined air-stripper and adsorption column results. These results were then compared to the initial time to component breakthrough data.

Calculation of the FMR until breakthrough of MTBE at 5μg/L =

$$((A_T-B_T) \times C_T)/ D_T \qquad \textbf{(eqn 4.4)}$$

Where A_T = Concentration of MTBE entering the air-stripper at a given point (μg/L), B_T = Concentration of MTBE in effluent of adsorption column (at Taguchi defined bed depth) at a given point (μg/L), C_T = Volume of water treated (L) and D_T = Total mass of MTBE present in the influent until component breakthrough at a given point (μg).

The volume of water treated until component breakthrough (applied to equation 4.4) was taken from the volume of water flowing through the adsorption column only. Although the air-stripper was run at a higher water flow rate than the adsorption column, generally the capacity of the air-stripper to remove MTBE or BTEX compounds will not alter at different water flow rates if the air-to-water ratio were changed accordingly. Note that this is an approximation only and does not take into account the difference in hydraulic properties that would be experienced within the air-stripping process if the air-to-water-ratio was altered. Note that the higher the FMR value calculated by equation 4.4, the better the removal efficiency of the remediation process.

Table 4.20 details the results required for the Taguchi analysis based upon time to component breakthrough and FMR.

Taguchi Run	Equivalent Experimental Run	Time until BT (Days)	FMR
1	2	1	0.21
2	7	2	0.47
3	3	1	0.92
4	5	1	0.66
5	8	13	0.73
6	6	3	0.58
7	1	1	0.66
8	4	1	0.29

Table 4.20. Results Table for Taguchi Runs 1-8.

Time to Component Breakthrough Summary.

Referring to table 4.20 it can be seen that in most cases the time until breakthrough of MTBE was day-1. Breakthrough for Taguchi tests 6 and 2 occurred on days 3 and 2 respectively. However, the time to breakthrough during Taguchi test 5 was 13 days. 13 days to component breakthrough was unusually high compared to the other results experienced throughout tests 1-8. This placed

considerable importance on the variables used throughout test 5. Note that other tests such as Taguchi Run 3 experienced breakthrough on day 1, yet the variables used suggested that the time to breakthrough should have been comparable to that of Run 5.

FMR Summary.

Referring to table 4.20 it can be seen that calculating the FMR until component breakthrough reduced the emphasis on Run 5, where the time until component breakthrough was far greater than any other breakthrough experienced. In general the range of values based upon FMR was greater than those based upon time to component breakthrough.

Using FMR, Taguchi Run 3 was identified as the most efficient remediation process.

Analysis of the Data.

Analysis of Mean (ANOM).

ANOM was carried out on both sets of results (time to component breakthrough and FMR) for each parameter.

Example Calculation.

To compute the mean value for BTEX Concentration at level 1, the performance results (or response) for the trials at level 1 were added and then divided by the number of such trials. Therefore referring to the BTEX Concentration column in Table 4.21, ANOM was carried out in the following manner;

BTEX Concentration - μg/L (lower level): (1+2+1+1)/4 = 1.25

BTEX Concentration - μg/L (upper level): (13+3+1+1)/4 = 4.5

Table 4.21 details the results and response based upon the time to component breakthrough. Note that the ANOM results highlighted in red denotes the optimum level combination.

BT Days	1 BTEX Conc. (µg/L)	2 MTBE Conc. (µg/L)	3 Q_A (L/min)	4 Q_W (L/min)	5 GAC BD (mm)	6 Packing BD (mm)	7 Carbon Type	Response
1	1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2	2
3	1	2	2	1	1	2	2	1
4	1	2	2	2	2	1	1	1
5	2	1	2	1	2	1	2	13
6	2	1	2	2	1	2	1	3
7	2	2	1	1	2	2	1	1
8	2	2	1	2	1	1	2	1
ANOM								Mean Response
Low	1.25	4.75	1.25	4	1.5	4	1.5	2.875
High	4.5	1	4.5	1.75	4.25	1.75	4.25	

Table 4.21. ANOM Analysis for Time to Component Breakthrough.

Table 4.22 details the results and response based upon FMR to component breakthrough. Note that the ANOM results highlighted in red denotes the optimum level combination.

FMR	1 BTEX Conc. (µg/L)	2 MTBE Conc. (µg/L)	3 Q_A (L/min)	4 Q_W (L/min)	5 GAC BD (mm)	6 Packing BD (mm)	7 Carbon Type	Response
1	1	1	1	1	1	1	1	0.21
2	1	1	1	2	2	2	2	0.47
3	1	2	2	1	1	2	2	0.92
4	1	2	2	2	2	1	1	0.66
5	2	1	2	1	2	1	2	0.73
6	2	1	2	2	1	2	1	0.58
7	2	2	1	1	2	2	1	0.66
8	2	2	1	2	1	1	2	0.29
ANOM								Mean Response
Low	0.57	0.50	0.41	0.63	0.50	0.47	0.53	0.57
High	0.57	0.63	0.72	0.50	0.63	0.66	0.60	

Table 4.22. ANOM Analysis fro FMR.

The ANOM results are expressed graphically in figures 4.67 – 4.68, where the characteristic quality of importance for the pilot-plant experiments centres around the average value for each of the factors being as large as possible.

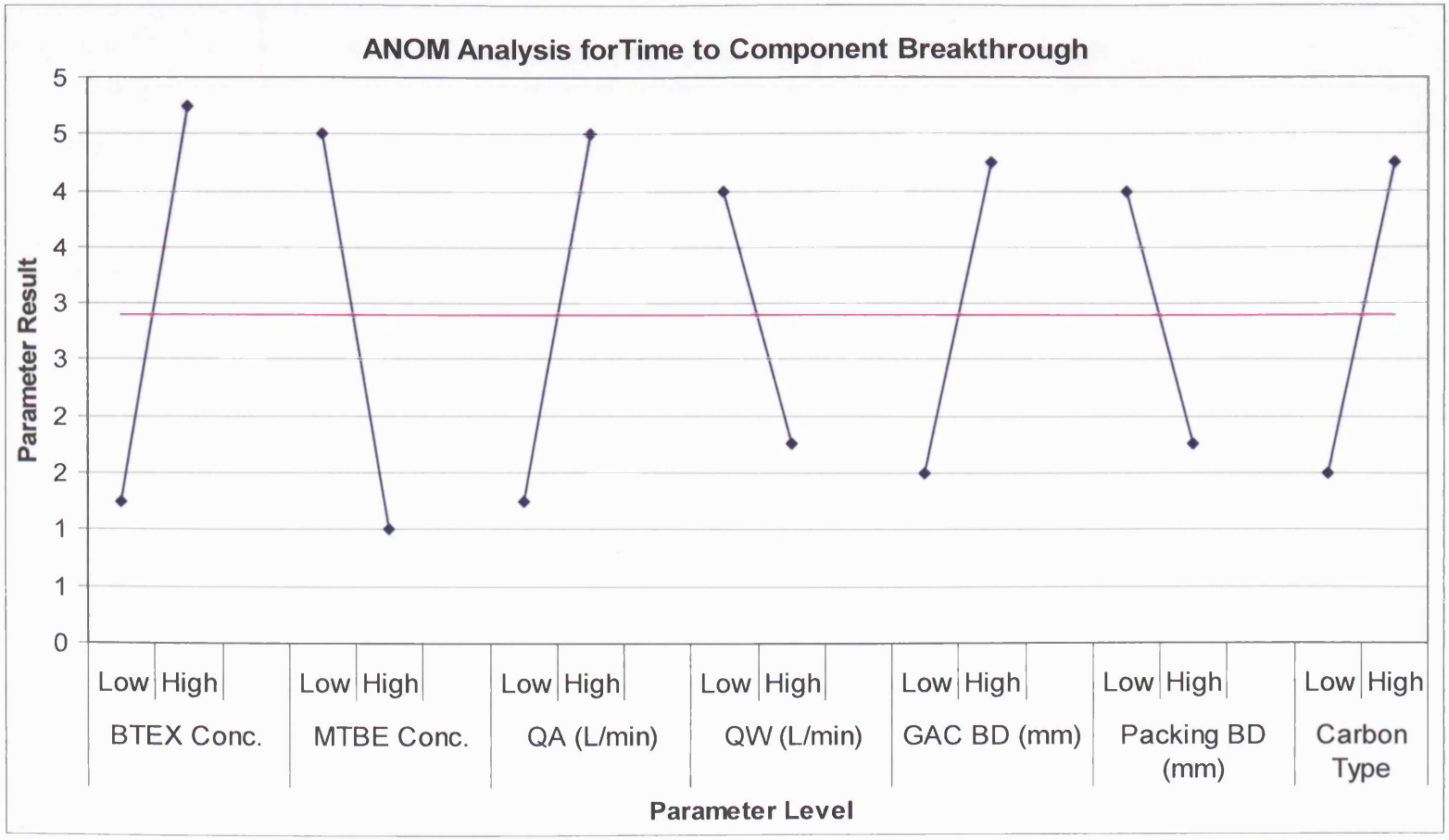


Figure 4.67. ANOM for Time to Component Breakthrough.

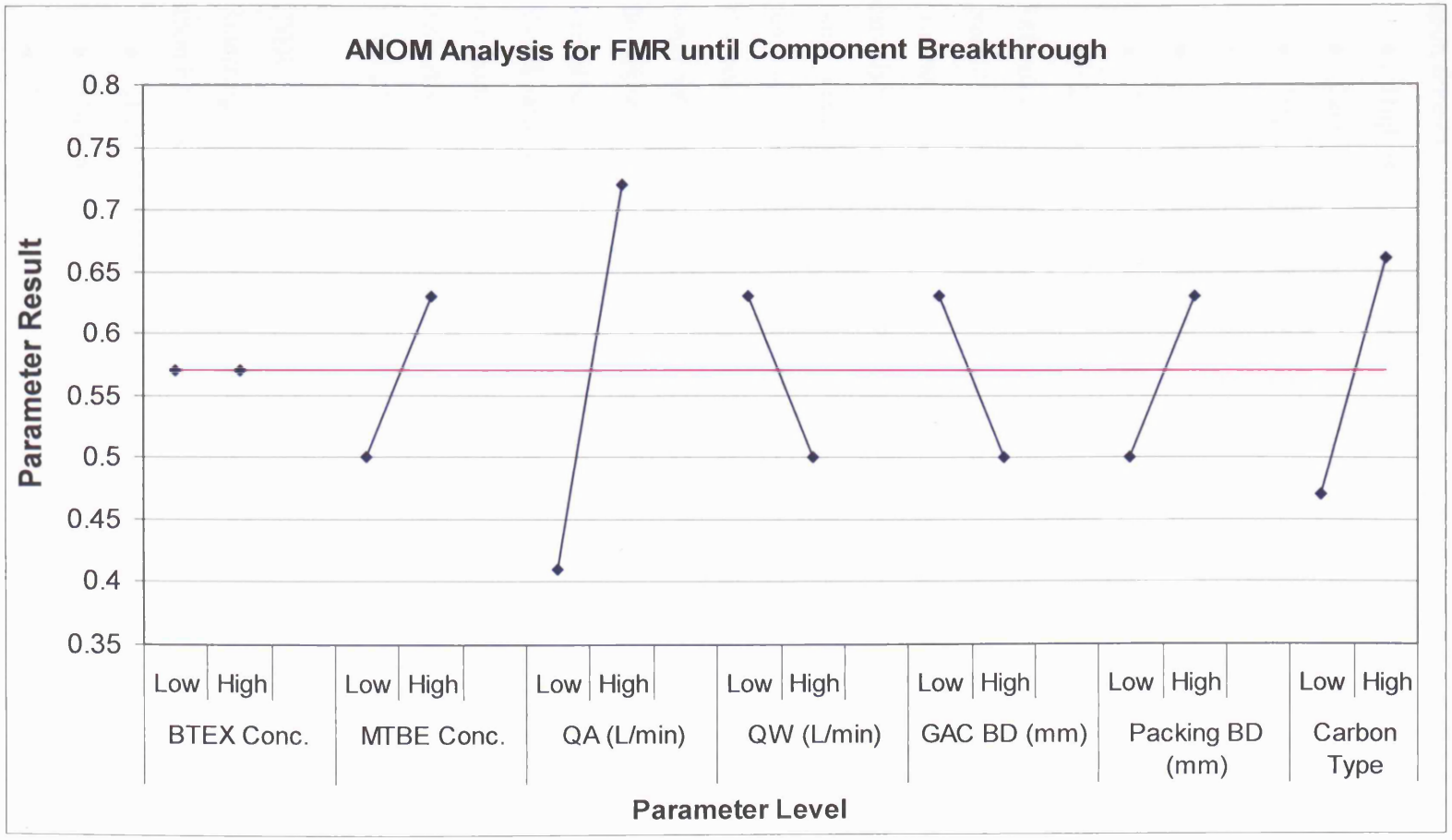


Figure 4.68. ANOM for FMR.

Time to Component Breakthrough.

Referring to Table 4.21 and Figure 4.67, the optimum process variables based upon time to component breakthrough are;

- High BTEX Concentration
- Low MTBE Concentration
- High Air Flow Rate
- Low Water Flow Rate
- High GAC Bed Depth
- Low Packing Bed Depth
- F600 Carbon

Referring to Figure 4.67 it can be noted that the upper and lower limits vary greatly from the mean. This places importance on implementing the correct process variable(s) in order to achieve the most robust process performance. It can also be noted that the performance results (both upper and lower) are of the same magnitude. For this reason the parameter(s) which have the greatest positive or negative effect cannot easily be identified.

The results indicate that implementing low MTBE concentrations, high air-to-water ratios and high GAC bed depth contribute positively to the robustness of the process performance. This follows the fundamental understanding of the air-stripping and adsorption processes. It does not follow that implementing a high BTEX influent concentration would contribute positively to extending the time to component breakthrough (rather than referring to relative capacities). Note that with ANOM analysis, F600 GAC was identified as contributing most positively to the process performance.

FMR

Referring to Table 4.22 and Figure 4.68, the optimum process variables based upon FME are;

- High MTBE Concentration
- High Air Flow Rate
- Low Water Flow Rate
- High GAC Bed Depth
- High Packing Depth

- F600 Carbon.

Referring to Figure 4.68 it can be noted that there is greater variance (above and below the mean) for the FMR parameter results, compared to those based upon time to component breakthrough. From Figure 4.68, the air flow rate can be identified as having the greatest effect on process robustness and should be set high. It can also be noted that the BTEX concentration makes the lowest contribution to the performance of the process.

The results indicate that implementing high air flow rates, low water flow rates, high GAC bed depths and high packing depth all contribute to process robustness. This follows the fundamental understanding of the air-stripping and adsorption processes. The ANOM analysis indicates that setting the MTBE concentration 'high' contributes positively to process robustness. Note from the ANOM analysis that the parameter results for the influent BTEX concentration cannot be identified and that both high and low influent concentrations leads to process robustness.

As discussed in Section 3.2.4 of Chapter 3, one limitation of a 2-level orthogonal array is that non-linear relationships, or the presence of maxima or minima's within the results, cannot be identified. These can only be identified using a minimum of a 3-level orthogonal array. Therefore the 'true' level at which the parameters should be set to achieve process robustness cannot be confirmed using the above ANOM analysis. However, the results do provide an indication of the preferred parameters.

Verification Test.

Although the Taguchi analysis calculated by FMR at breakthrough provided more reliable results than using time to component breakthrough, the verification test was formulated using the time to component breakthrough. This was because the FMR calculation was devised only after the results of the experiments had been fully investigated.

Referring to Section 3.2.4 of Chapter 3, the aim of the verification test was to confirm the results suggested by the Taguchi analysis. By setting the variables at the optimum values indicated, the time to component breakthrough should be maximised. If the verification test confirms that the variables indicated by the Taguchi analysis maximise the time to breakthrough, then these variables should

be adopted as the design blueprint for a remediation unit. If the variables indicated by the Taguchi analysis do not show process optimisation upon completion of the verification test, then the experiments should be reformulated and the experimental process started again from the beginning.

Referring to table 4.21, the most positive value for each parameter was set as the limit for the purpose of the verification test.

Following this method the verification test was formulated and is detailed in table 4.23.

VARIABLES						
1	2	3	4	5	6	7
BTEX Conc.	MTBE Conc.	Q_A	Q_W	GAC BD	Packing BD	Carbon Type
2	1	2	1	2	1	2

Table 4.23. Variables used for Verification Run, as Calculated by Taguchi Analysis.

Note that the variables indicated by the Taguchi analysis are identical to the variables used for Run 5.

Table 4.24 details the average influent concentration, time until breakthrough and FMR at component breakthrough for Run 5 and the verification test (previously referred to as Run 8 Repeat).

RUN	Av. Influent (µg/L)	Time until BT (Days)	FMR
5	13	13	0.73
Verification	10	8	0.60

Table 4.24. Comparison of Data from Taguchi Run 5 and the Verification Test.

Referring to table 4.24 it can be seen that the average influent concentration of MTBE for Taguchi Run 5 and the verification test was 13 and 10µg/L respectively. This suggested reasonable inter-test repeatability.

The time to component breakthrough for Run 5 was 13 days, whilst the time to component breakthrough for the verification test was 8 days. Although breakthrough in the verification test was earlier than in Run 8, breakthrough at day 8 was still greater than those experienced throughout the remainder of experiments 1-8. Based upon the time to breakthrough this suggests that the variables selected for Run 5 and the verification test were close to optimum process conditions (based upon a 2-level orthogonal array only). If the verification test confirmed what was suggested by the initial ANOM analysis, then the variables adopted for the particular test should be implemented as the optimum process parameters.

When considering the FMR values at the time of component breakthrough, it can be seen that the FMR for Run 8 and the verification test was 0.73 and 0.60 respectively. Although these figures are not the same, they are reasonably similar. Again this suggests that the variables used throughout Run 5 and the verification test were close to the optimum settings. However, when the FMRs are compared to the other FMR values detailed in table 4.20 it can be seen that Taguchi Run 5 and the Verification test no longer had the greatest value. For example Run 3 gave a FMR value of 0.92, whilst Runs 4 and 7 produced comparable FMR values to those of Run 8 and the Verification test.

Summary of Implementation of Taguchi Method.

The Taguchi ANOM analysis based upon FMR seemed to provide the most reliable results based upon the fundamentals of the air-stripping and adsorption processes. That is; high air-to-water ratios, high GAC bed depth, high packing depth and F600 GAC. The Taguchi analysis based upon FMR at component breakthrough suggested the parameters implemented throughout Run 3 were close to the optimum process variables (rather than Run 5 based upon time to component breakthrough). The air-to-water ratio was identified as the parameter which had the greatest effect on process robustness. Calculating the FMR at component breakthrough was successful in reducing the emphasis of the results from Run 5. Note that the Verification test was formulated on the results given by time to component breakthrough, as it was only after interpretation of the full set of results that the FMR calculation was devised. For this reason optimum design variables based upon FMR cannot be verified.

Since the fluctuating influent concentration influenced the time to component breakthrough, the Taguchi analysis based upon time to breakthrough was effectively invalid. However, the verification test based upon time to component breakthrough did suggest that the variables implemented in Run 5 were optimum for process robustness. Unless the problem with the fluctuating influent concentration can be solved, Taguchi analysis should not be implemented for experiments such as those implemented in the present study.

The ANOM analysis performed throughout the Taguchi method was based upon a 2-level orthogonal array, hence only a linear relationship can be observed. Without implementing a 3-level orthogonal array, the presence of maxima's or minima's within the graphical presentation of the ANOM cannot be ruled out. As previously stated, a 3-level orthogonal array was not implemented in the present study as the number of variables that could be tested on the pilot-plant would have been too small.

4.5. Summary of Experimental Trials.

The following section presents a summary of the experimental trials.

Air-Stripping.

The highest removal efficiency of benzene throughout the experimental trials was 90% and the highest removal efficiency of MTBE was 89%. However referring to Table 4.7, the experimental trials showed that generally the removal efficiency of benzene was greater than that of MTBE. This concurred with a review of the literature in which it was stated that MTBE was not amenable to air-stripping due to its physiochemical properties.

The highest removal efficiency of benzene occurred when the air-to-water ratio was low (12) and the influent concentration was high (average 135µg/L). The highest removal efficiency of MTBE occurred when the air-to-water ratio was high (86) and the influent concentration was medium to high (67µg/L). This concurs with literature in which Roberts *et al* (1985) suggested that for volatile compounds (e.g. benzene), mass transfer within an air-stripping column was independent of the air flow rate. Given that high influent concentrations were experienced throughout Run 1, the overall mass transfer and ARE% was high. It was also suggested in literature that for less volatile compounds (e.g. MTBE) the mass transfer coefficient decreased with decreasing air flow rates.

Based upon the data presented in Table 4.7, for both benzene and MTBE the packed height did not seem to affect the ARE% values. This concurs with literature in which Roberts *et al* (1985) suggested that the packed height (Z) had relatively little effect on the mass transfer coefficient. Referring to equations 1.10 – 1.13 it can be observed that the mass transfer coefficient (K_La) is independent of packed height.

The air-stripping trials were affected by the variable influent concentrations. Generally for MTBE as the influent concentration increased, the effluent concentration increased. Given that benzene was more amenable to air-stripping, the effluent concentration was generally affected less by the variable influent concentration.

Note that throughout the experimental trials, the remediation targets for benzene and MTBE were not met, even though in some instances (for e.g. Run 6, 7 and 8)

the average effluent concentrations were below the remedial targets. This was caused by the variable influent concentration.

Adsorption Column.

Throughout the adsorption column trials, generally the removal of benzene was greater than that of MTBE. This can be observed in Tables 4.17 – 4.19 where the ARE%, breakthrough and capacity data suggested more favourable adsorption for benzene. This concurs with literature which suggested that benzene would be more amenable to adsorption than MTBE due to its physiochemical properties (for example lower solubility).

Referring to Table 4.17 the greatest adsorption capacity with respect to both compounds occurred in Run 1 for MTBE (3.45mg/g). This was the only occasion where the capacity was greater for MTBE than it was for benzene. However, referring to Run 1 the influent concentration of MTBE was much greater than that of benzene. It was expected that low influent concentrations should yield lower capacities than higher influent concentrations; therefore it is feasible therefore that at higher influent concentrations, MTBE may show a greater adsorption capacity than benzene. Note that the ARE% and breakthrough data throughout Run 1 was still greater for benzene than it was for MTBE.

Referring to Runs 2, 3 and 6 where the influent concentration of MTBE and benzene were similar, competitive adsorption can be observed. Benzene effectively out-competes MTBE for the pore sites within the GAC. Competitive adsorption of compounds more amenable to adsorption (e.g. benzene) is well documented in literature. Note that benzene was not only competing with MTBE for the pore sites, but with the remainder of the TEX compounds and any other organics within the influent water (e.g. BOM).

The experimental trials were not conclusive as to whether F400 or F600 carbon provided the most favourable adsorption of an MTBE – BTEX mixture. Certainly the results for F400 and F600 were comparable. However, it can be noted that the greatest adsorption capacity experienced throughout the experimental trials (for both MTBE and benzene) was for F400 carbon (Run 1).

The adsorption trials were severely affected by the variable influent concentration. Generally as the influent concentration increased, the effluent concentrations for each bed depths also increased. For this reason data such as

time to component breakthrough should be discounted. The graphs showing the fraction of MTBE and benzene passing through the carbon were designed to overcome the variable influent concentration. However, throughout the experimental trials it can be noted that the influent concentration still affected the quality of the results. Typical breakthrough curves similar to those presented in Section 1.6.2.6.2 of Chapter 1 (Figure 1.12) were not experienced throughout the trials.

The mass adsorbed for the duration of the adsorption trials and the adsorptive capacity data took into account the variable influent concentration, although it should be noted that the carbon was not tested until exhaustion.

It can be noted that desorption of MTBE and benzene sometime occurred (for example Run 8 Repeat). It is possible that at low influent concentrations, equilibrium is achieved between the influent and effluent, hence leading to desorption of the adsorbate back into solution. When desorption occurs towards the end of the tests (e.g. Run 4 benzene), this suggests that equilibrium between the influent and effluent has occurred.

Taguchi Analysis

A summary of the implementation of the Taguchi Orthogonal Method can be found in Section 4.4.

It was suggested in the summary that the Taguchi analysis based upon time to component breakthrough was affected by the variable influent concentration and therefore should not be viewed as conclusive. The Taguchi analysis based upon FMR took into account the variable influent concentration, however the calculations were made retrospectively and hence a verification test could not be carried out.

Given that a 2-level orthogonal array was implemented in order to test as many variables on the pilot-plant as possible, the ANOM data expressed graphically in Figures 4.67 and 4.68 do not include the possibility of non-linear trends.

Note that the Taguchi analysis based upon time to component breakthrough and FMR both suggest that F600 carbon was more favourable than F400 carbon. This does not concur with the limited findings of the individual air-stripping and adsorption trials.

CHAPTER 5: DISCUSSION.

The aim of the discussion chapter is to relate the performance of the pilot-plant trials to literature presented in Chapter 1.

5.1. Air-Stripping Discussion.

The results of the air-stripping trials are compared to those presented in the literature review in terms of ARE%. Where possible, process performance is related to the influent concentration of MTBE and BTEX compounds and air-to-water ratios.

The variables implemented throughout the experimental phase and the ARE% achieved for the fuel oil trials are summarised as follows;

- Influent concentration of MTBE 6μg/L - 175μg/L
- Influent concentration of Benzene 28μg/L - 164μg/L
- Air-to-water ratios 9 – 86
- ARE% MTBE 20 – 89%
- ARE% Benzene 52 – 90%.

First to note is that generally the air-to-water ratios implemented in literature were greater than those used throughout the experimental trials. For example Gerbasi and Memoli (1994) suggested that air-to-water ratios greater than 100 would be needed to remove MTBE from contaminated groundwater. Whilst Shih *et al* (2003) suggested that air-to-water ratios would need to be 6 times that required for other petroleum compounds such as benzene in order to strip MTBE. The ARE% experienced throughout the experimental trials for MTBE ranged from 20 – 89%. The median MTBE ARE% throughout the experimental trials was 41%.

The American Petroleum Institute (API) evaluated the performance of MTBE removal during air-stripping for a total of 57 contaminated sites within the US. They found that MTBE removal efficiencies ranged from 55% to 100% for 15 of the sites investigated (Burgess *et al*, 1998). It can be noted that the removal efficiencies experienced in the study carried out by Burgess *et al* (1998) were greater than those experienced in the present study. Complete removal of MTBE was experienced in the US study. Without knowing the air-to-water ratios implemented in the API study it is difficult to compare exactly the studies. An

ARE% of 89% was achieved in the present study with an air-to-water ratio of 86, suggesting that at slightly higher ratios, air-stripping can be utilised as an effective remediation technology for MTBE.

Safarzadeh-Amiri (2001) suggested that the implementation of air-stripping technology to remediate MTBE would require an air-to-water ratio greater than 200 to produce an MTBE removal rate of 95%. The 95% removal efficiency suggested by Safarzadeh-Amiri (2001) was higher than those experienced in the present study. An ARE% of 89% was achieved in the present study, however this was achieved using a much lower air-to-water ratio of 86.

Sutherland *et al* (2004) conducted air-stripping experiments for five different groundwater sites, each with varying MTBE influent concentrations. Air-to-water ratios of 75:1, 100:1 and 150:1 were implemented throughout the study. Sutherland *et al* (2004) suggested that the MTBE mass transfer coefficients derived from the experimental data were low for each groundwater at each air-to-water. This was attributed to the low Henry's Law Constant and high solubility of MTBE. Low mass transfer coefficients were also experienced within the present study compared to those of more volatile compounds. Sutherland *et al* (2004) suggested that for each groundwater, greater air-to-water ratios correlated with increased mass transfer for MTBE. This was also noted in the present study, where increases in air-to-water ratios correlated with increased ARE% and mass transfer coefficients for MTBE.

Referring to the present study this was not the case for benzene, where increases in air-to-water ratios did not necessarily correlate with increased mass transfer coefficients. Roberts *et al* (1985) suggested that for volatile compounds such as benzene, mass transfer was independent of the air and water flow rates (i.e. air-to-water ratios). For less volatile solutes including MTBE, the observed mass transfer decreased with decreasing air and water flow rates.

Sutherland *et al* (2004) calculated the required tower height for each groundwater application in order to achieve removal efficiencies of 80 and 99.5%. It was found that due to the low mass transfer coefficients, the tower heights required to achieve 80 and 99.5% removal efficiencies were uneconomical and in some cases would have to be up to 24m in height.

Stover and Kincannon (1983) studied the removal of VOCs including benzene, toluene and ethylbenzene (BTE) compounds in a laboratory scale test rig. The parameters and results are summarised below;

- Influent concentration of benzene – 68.8μg/L
- Influent concentration of toluene – 92.0μg/L
- Influent concentration of ethylbenzene – 23.5μg/L
- Air-to-water ratios 9 – 396
- ARE% benzene 0 – 48%
- ARE% toluene 51 – 93%
- ARE% ethylbenzene 96 – 100%.

Referring to the study conducted by Stover and Kincannon (1983), the influent concentrations were similar to those implemented throughout the present study. Referring to Table 1.15 the air-to-water ratios implemented were also similar, although the upper air-to-water ratio was significantly higher in the study carried out by Stover and Kincannon (1983) (396). First to note is that there were no reliable toluene and ethylbenzene results in the present study due to the GC-MS procedure.

The removal efficiency of benzene in the present study was far greater than that implemented in the Stover and Kincannon (1983) study. The lowest removal efficiency experienced in the present study (52%) corresponded to the highest removal efficiency experienced in the Stover and Kincannon (1983) experiments (48%). Note that the highest removal efficiency of 48% experienced in the study conducted by Stover and Kincannon (1983) was achieved using an air-to-water ratio of 396. At low air-to-water ratios (9 and 26), removal did not occur at all for benzene. 7mm Raschig rings were utilised as the packing material within the Stover and Kincannon (1983) air-stripping experiments. A comparison between the removal efficiencies experienced in both studies suggests that the stainless steel structured packing utilised in the present study was far more efficient than the traditional random packing (Raschig rings). This agrees with what literature suggested with respect to the higher theoretical removal efficiency of structured packing (section 1.5.3.1 of Chapter 1).

Throughout literature it is stated that the Henry's Law Constant is the effective driving force behind the air-stripping process (e.g. Keller *et al,* 2000 and Munz

and Roberts, 1987). Due to the fact that MTBE has a lower Henry's Law Constant than benzene, it was suggested that it would be less amenable to air-stripping than benzene. Overall, the present study results agreed with literature in which it was suggested that MTBE would not be as amenable to air-stripping as benzene.

Based upon limited experimental trials, the results from the present study suggest that structured packing is more efficient than random packing in the removal of benzene. With respect to MTBE, the removal efficiency is dependent upon the air-to-water ratio and should be implemented at ratios no less than 90:1 in order to achieve removal efficiencies of approximately 90%.

The results of the experimental trial agreed with literature in that for volatile compounds such as benzene, mass transfer is not dependent upon packing height or the air-to-water ratio.

5.2. Adsorption Column Discussion.

The results of the adsorption trials are compared to those presented in the literature review in terms of adsorptive capacity (mg/g). Where possible, process performance is related to the influent concentration of MTBE and BTEX compounds and carbon type. Note that although data such as ARE% and time to component breakthrough was presented in Chapter 4, the data has not been used to compare the present study results with literature.

The variables implemented throughout the experimental phase and the adsorptive capacity achieved are summarised as follows;

- Influent concentration of MTBE 3.4μg/L - 93μg/L
- Influent concentration of Benzene 5.1μg/L - 23μg/L
- Carbon type – F400 and F600 (Calgon Carbon Company)
- Capacity F400 MTBE - 3.45 mg/g, F400 Benzene 2.72 mg/g
- Capacity F600 MTBE - 1.45 mg/g, F600 Benzene 1.96 mg/g.

Note from section 4.3 of Chapter 4 that there is limited data available for F600 carbon due to selective degradation during storage. Also, the lower benzene influent concentrations experienced in the adsorption trials reflect the fact that the air-stripper (which provided the influent concentration) was more effective at removing benzene than it was MTBE.

The USEPA suggested that GAC is approximately 1/3 – 1/8 as effective in removing MTBE as it is benzene from contaminated groundwater (USEPA, 1998). It is assumed that the concentration of MTBE and benzene in the influent were similar when referring to the USEPA data. Referring to the present study on the whole, the results suggest that the adsorption of benzene is much greater than that of MTBE. In some cases the effectiveness of carbon in removing benzene as supposed to MTBE is greater than a factor of 8. Run 1 suggests that the adsorptive capacity of F400 for benzene and MTBE are equivalent. However, the influent concentration of MTBE was much greater than benzene throughout Run 1.

The American Petroleum Institute (API) reports a GAC capacity of 4mg/g for MTBE and 300mg/g for benzene (Burgess *et al* 1998). Assuming that the influent concentrations of MTBE and benzene were similar, this highlights the fact that benzene is much more amenable to adsorption than MTBE. The highest adsorptive capacity for MTBE throughout the present study was 3.45mg/g, which was comparable to that suggested by the API. The highest adsorptive capacity for benzene throughout the present study was 2.72mg/g, which was an order of magnitude less than that suggested by the API. Note however that the influent concentration used in the API study was not cited and that the GAC implemented throughout the present study were not tested to complete exhaustion. It is possible that much higher influent concentrations of benzene and MTBE were implemented in the studies cited by the API, which would translate into much higher adsorptive capacities. Although the data presented in the present study indicated that the adsorptive capacities for MTBE and benzene were similar (3.45mg/g and 2.72mg/g respectively), referring to tables 4.17 – 4.18, GAC was seen to be much more amenable to the adsorption of benzene.

Sutherland *et al* (2004) studied the GAC removal of MTBE (in the presence of BTEX compounds) from 5 contaminated groundwaters. The parameters and results are summarised below;

- Influent concentration of MTBE in F400 trials 0.023 – 5.03 mg/L
- Influent concentration of MTBE in F600 trials 0.029 – 5.31 mg/L
- Total capacity F400 9.3 mg/g
- Total capacity F600 19.94 mg/g.

Note that the influent concentrations of MTBE in the study conducted by Sutherland *et al* (2004) were much higher than those experienced in the present study.

Referring to the present study the capacity of F400 carbon was 3.45 mg/g, which although was less than that experienced in the study conducted by Sutherland *et al* (2004) (9.3 mg/g), was certainly comparable. However referring to F600 GAC the MTBE capacity achieved in the present study was 1.45 mg/kg, whilst the capacity achieved throughout the study conducted by Sutherland *et al* (2004) was 19.94 mg/g. This was clearly much higher than that experienced in the present study. Referring to Table 1.16 the influent concentration of MTBE was much higher in the Sutherland *et al* (2004) study. It is known that the carbon in a GAC column comes to approximate equilibrium with the influent water, therefore high influent concentrations should yield high capacities. It is possible that the higher adsorptive capacities experienced throughout the Sutherland *et al* (2004) study were caused by the high influent concentrations. Note from Table 1.16 and 4.18 – 4.18 that when the influent concentrations were similar in both studies, the capacities for both F400 and F600 GAC were similar.

Davis and Powers (2000) studied the adsorptive capacity of a number of different alternative adsorbents in removing MTBE and gasoline contaminants from groundwater. Sorbents included; synthetic carbonaceous resins, porous graphitic carbon, C_{18} silicas and acrylic resins. F400 GAC was also tested for comparison purposes. The results are summarised below;

- Total capacity F400 - 3.1 mg/g
- Total capacity Ambersorb 563 - 16.2 mg/g
- Total capacity Ambersorb 572 - 13.8 mg/g
- Total capacity Hypercarb - 6.5 mg/g
- Total capacity Polysorb MP-1 - 0.8 mg/g

Referring to the present study, the total capacity for F400 carbon to adsorb MTBE (3.45 mg/g) was similar to that experienced in the study conducted by Davis and Powers (2000) (3.1 mg/g). The capacity for F400 to adsorb MTBE throughout the present study was also similar to that of the Hypercarb adsorbent (6.5 mg/g) and indeed much higher than that of the Polysorb MP-1 adsorbent (0.8 mg/g). Note that the capacities for the Ambersorb carbonaceous resins were

higher than the capacity for the F400 carbon. Davis and Powers (2000) suggested that at an equilibrium concentration of 1 mg/L and when no other contaminants were present, Ambersorb 563 was found to have five times the adsorptive capacity of F400 GAC in removing MTBE. When m-xylene (a representative gasoline compound) was added to the solution, this increased to six times the capacity of F400. Note that the present study included the influence of BTEX compounds in MTBE adsorption. Although carbonaceous resins clearly have higher adsorptive capacities than F400, they have not yet gained regulatory approval for use in the world-wide water industry. It should be noted that the influent concentrations were much higher in the Davis and Powers (2000) study.

Shih *et al*, 2003 evaluated the use of GAC types on the removal of MTBE from both a groundwater source and a surface water source. The aim of the study was to validate and optimise GAC performance in removing MTBE in the presence of BTX, NOM and breakdown products of MTBE (e.g. TBA). Two types of coconut-based GACs were used within the study; PCB (produced by Calgon Carbon) and CC602 (produced by US Filter). Carbon capacities were made based upon their performance in removing MTBE from a surface water lake. The variables implemented throughout the experimental phase and the capacity achieved are summarised as follows;

- Influent concentration of MTBE = 20 μg/L
- Influent concentration of Benzene = 108 μg/L
- Influent concentration of p-xylene = 97 μg/L and
- Influent concentration of TBA = 100 μg/L
- Total capacity CC – 602 (EBCT 10 mins) = 0.110 mg/g
- Total capacity CC – 602 (EBCT 20 mins) = 0.186 mg/g
- Total capacity PCB (EBCT 10 mins) = 0.142 mg/g
- Total capacity PCB (EBCT 20 mins) = 0.217 mg/g

It can be noted that the influent concentration of MTBE and benzene were similar throughout the present study and the study conducted by Shih *et al* (2003). Referring to the present study it can be noted that the total capacity of both F400 and F600 GAC was greater than those experienced in the Shih *et al* (2003) study. In some cases the capacity of F400 and F600 GAC were greater than the capacity of PCB and CC – 602 GAC by an order of magnitude. This

suggests that F400 and F600 GAC should be implemented as a carbon of choice ahead of PCB and CC – 602 GAC.

A comparison of the adsorptive capacities between the present experimental trials and those cited within literature has not been conclusive as to which adsorbent may be more effective in the remediation of MTBE and benzene. Section 5.2 of Chapter 5 suggests that in some instances the capacities experienced in the present trials were much less than those cited in literature. However, the studies cited within literature were conducted at much higher influent concentrations. At higher influent concentrations, higher capacities can be expected. Alternative adsorbents appear to have much higher capacities than GAC, however they have not yet gained regulatory approval for use in the water industry.

Sutherland *et al* (2004) suggested that for all groundwaters tested within their study, F600 carbon showed significantly greater breakthrough and ultimate capacities than F400 for MTBE by a factor of 1.5 – 2. It can be noted that within the present study this was not the case, where the capacity of F400 was generally greater than that of F600. However, the highest capacity achieved throughout the Sutherland *et al* (2004) study occurred when BTEX compounds were not present. An MTBE - BTEX contaminant mixture was implemented throughout the present study, suggesting that the differences in the relative performance of F400 and F600 GAC could have been caused by the competitive effects of MTBE and BTEX compounds.

The results of the present study agreed with literature in which it was suggested that benzene was more amenable to adsorption than MTBE and that competitive adsorption plays an active role in the remediation of fuel oil compounds from contaminated water.

Shih *et al* (2003) suggested that GAC performance was greatly reduced in the presence of total organic carbon (TOC). The influence of TOC and BOM has not been quantified within the present study, but is likely to have an effect on the overall performance of the carbon.

5.3. Comparison of Experimental Trials with AOPs.

Section 1.5 of Chapter 1 suggested that AOPs could be implemented as post-abstraction remediation technologies and that the technology was effective at removing MTBE and BTEX compounds from contaminated groundwater.

Air-stripping can be compared to AOPs in terms of ARE%. The ARE% achieved in the air-stripping trials ranged from 20 – 89% for MTBE and 52 – 90% for benzene. Influent concentrations of MTBE ranged from 6μg/L - 175μg/L whilst influent concentrations of benzene ranged from 28μg/L - 164μg/L It is harder to compare the adsorption column results to AOP literature, due to the fact that the adsorption is cited in literature in terms of capacity (mg/g), whilst AOP is cited in terms of removal efficiency. However, ARE% was calculated for the adsorption trials and are presented in Tables 4.17 – 4.18. Where possible ARE% is compared to the removal efficiency of AOPs.

Graham *et al* (2002) suggested that based upon an MTBE influent concentration of 1200μg/L, the removal efficiency for ozone AOP was 97.5%, whilst the removal efficiency for UV-ozone AOP was 99.95%. Even at higher influent concentrations it can be noted that the removal efficiency of ozone and UV-ozone AOP was greater than the efficiency experienced in the air-stripping trials. Referring to Tables 4.17 – 4.18 comparable removal efficiencies for the adsorption trials were achieved, but these corresponded to higher bed depths. The ARE% at lower bed depths (especially for MTBE) were generally much less than the removal efficiencies suggested by Graham *et al* (2002). However, as with other AOPs a number of by-products were produced in the Graham *et al* (2002) study which included; *t*-Butyl-formate (TBF), methyl acetate, butane, acetone and acetaldehyde.

Chang and Young (2000) suggested that at MTBE influent concentrations of approximately 10mg/L, nearly complete removal of MTBE (99.9%) could be achieved using an ozone - peroxide (UV/H_2O_2) treatment process. However, it was observed that as the concentration of MTBE decreased, the concentration of the by-product TBF also increased. At benzene influent concentrations of approximately 500μg/L, removal efficiencies of up to 99.9% were also achieved. Again, as with the ozone and UV-ozone AOPs, ozone- peroxide AOPs seem to be more efficient in benzene and MTBE removal than air-stripping and adsorption.

It can be noted that referring to section 2.2 of Chapter 2, MTBE influent concentrations of 10mg/L are not indicative of contaminated groundwaters, in both the US or Europe. In order to provide a direct comparison, experiments should be run with similar influent concentrations.

Burbano *et al* (2003) suggested that Fenton's Reagent (FR) had been used successfully in the removal of MTBE from water, with influent concentrations ranging from 1-2 mg/L. Under certain reaction conditions, removal efficiencies of 99.9% had been achieved using FR, but complete mineralisation had not been achieved. Also, *t*- Butyl-alcohol (TBA), TBF, methyl acetate and acetone were identified as process by -products. As with the other AOP treatments discussed in this section AOP using FR had achieved removal efficiencies greater than that experienced in the air-stripping and adsorption trials.

Mitani *et al* (2002) suggested that although air-stripping and GAC systems cost less to install and run than AOP systems, AOP had the advantage of not requiring an additional treatment step for the disposal of the pollutant. However as with all AOP processes cited within literature, harmful by-products such as TBF and TBA are formed by the incomplete oxidation of MTBE. TBF and TBA may pose a greater risk than health MTBE itself. Given that the remediation options tested in the present study were designed to be implemented at a PWS borehole after a contamination event, the production of compounds more harmful than the initial pollutant does not seem advantageous to a remediation option.

Shih *et al* (2003) also suggested that although advanced oxidation could be used in the removal of contaminants from water, harmful by-products such as bromate could be produced and hence would require additional removal before the water is distributed. One of the advantages of implementing AOPs is that complete removal of the pollutant can occur and that the process does not just transfer pollutants from one phase to another. However, if harmful by-products are produced, again this does not seem advantageous to the remediation of contaminated groundwater for drinking water supplies.

5.4. Impact of Influent Variability on Results.

It can be observed throughout the Chapter 4 that both the air-stripping and adsorption column results were affected by the variable influent concentration. The impact of the variable influent concentration is discussed on an experiment by experiment basis throughout Chapter 4 and is also summarised in section 4.5. The variability of the influent concentration not only made the interpretation of the results more difficult, but also meant that the results produced in the experimental trials were subject to unquantifiable errors. Care was therefore taken when comparing the results of the present study with relevant literature.

Referring to the air-stripping results it can be seen that generally as the influent concentration increased and decreased, the effluent concentration responded by increasing and decreasing. In turn it was difficult to interpret the influence of the influent concentration on the process performance, because of its variability. This can also be said for the adsorption column results. In general (and particularly for MTBE) as the influent concentration increased, the effluent concentration also increased. This in turn meant that data such as time to component breakthrough was effectively invalid. The problems associated with variable influent concentration on adsorption trials have also been documented in literature (Hand *et al*, 1989).

Attempts were made when interpreting the data to express the results independently from the influent concentrations. For the air-stripping column this included calculating the removal efficiency on a point by point basis and averaging the efficiency for the entire test (ARE%). The removal efficiency data was also expressed graphically along with the variable influent concentration. ARE% was also calculated for the adsorption results, along with the capacity of the carbon at breakthrough and for the entire test. Although desorption towards the end of some of the trials suggested that equilibrium had been achieved, it is not known whether total (or ultimate) capacity of the carbon had been attained throughout the experiments. In order to express the results graphically, the fraction of MTBE and BTEX passing through the carbon was plotted against time. This method is used throughout literature to express the results independently from the influent concentration.

Referring to Chapter 4, even with the addition of the interpretative calculations, the results were still affected by the variability in the influent concentration.

The overall quality of the data could be improved if a sampling regime were adopted in which samples were tested multiple times throughout the day. This would give a more accurate picture of the variable influent concentration. Also, breakthrough in the carbon bed would be detected 'as it happens' hence the GAC adsorptive data would be more valid.

Influent (and effluent) variation throughout the present study may have been caused to some extent by the storage of the samples. It is certainly known that benzene degradation occurred during Runs 7 and 8. If a dedicated GC-MS resource were available to future experimental trials, sample storage would then not be required and hence would not be subjected to chemical degradation.

Given the problems associated with the variable influent concentration throughout the fuel oil tests, there are a number of changes that could be made to the experimental method in future trials. Firstly, the air-stripping and adsorption column experiments should be separated. This would mean that the influent concentration to the adsorption column could be controlled accurately and would not be influenced by the efficiency of the air-stripping column.

Air-stripping experiments do not need to be run continuously for extended periods of time in order to gain information such as ARE%. A large batch tank of equilibrated MTBE-BTEX solution (of a known concentration) could be used to feed the air-stripping column alone, for shorter experimental periods. If periodic samples taken from the batch tank indicated a fall in MTBE - BTEX concentration, then more solution could be added to the tank when necessary. Using a large batch tank system would increase the number of air-stripping trials that could be run. Also, the conclusion of the experiments would not be dependent upon achieving breakthrough within the adsorption column.

It was evident from the adsorption column results that GAC capacity was dependent on the influent concentration. A batch tank system could also be implemented for the adsorption column trials, where adsorptive capacity could be tested over known influent concentrations. Again, the MTBE - BTEX solution within the batching tank could be monitored and more solution added if necessary.

Changes to the overall test rig could include replacing the Perspex air-stripping and adsorption columns to glass or stainless steel in order to minimise the possible adsorption of organics to the columns.

CHAPTER 6: CONCLUSIONS.

The aim of Chapter 6 is to conclude the present study with respect to the project aims and objectives and the findings of the experimental phase. The aims and objectives are presented in Chapter 2 whilst the experimental results and findings are presented in Chapter 4 and 5 respectively.

It was the aim of the present study to provide an indication of an optimised remediation strategy for the simultaneous removal of MTBE and BTEX compounds from groundwater. Remediation was investigated utilising air-stripping and GAC columns in series. Remedial targets for MTBE and benzene corresponded to the most stringent world-wide targets. With respect to benzene this was set at 1μg/L, whilst the remediation target for MTBE was 5μg/L. Influent concentrations of MTBE and BTEX compounds represented levels likely to be found in contaminated groundwater (section 2.2 of Chapter 2).

Stainless steel structured packing was implemented as the packing material within the air-stripper, as this type was cited in literature as having a higher theoretical removal efficiency than traditional random packing. F400 GAC was utilised within the adsorption column as this represented a commonly accepted carbon, implemented throughout the world-wide water industry. F600 GAC is a relatively new product specifically designed to remove trace organics, in particular MTBE.

The experimental phase of the present study implemented air-stripping and adsorption column technology and was carried out on laboratory-scale pilot-plant apparatus.

Air-stripping removal efficiencies for MTBE ranged from 20 – 89% and was found to be dependent upon the air-to-water ratio implemented. That is, the removal efficiency increased as the air-to-water ratio was increased. This follows literature in that for less volatile compounds (i.e. MTBE), mass transfer and hence removal efficiency was dependent upon air-to-water ratios. Air-stripper removal efficiencies for benzene ranged from 52 – 90%. Note that the median air-stripping removal efficiency values differed greatly. For MTBE the median value was 41%, whilst the median removal efficiency value for benzene was 81%. This suggests that benzene is much more amenable to air-stripping than MTBE. The removal efficiency of benzene was found to be independent on the air-to-water ratio and the packing height implemented. Again this agrees with

literature in which for volatile compounds (e.g. benzene), mass transfer and hence removal efficiency were independent of air-to-water ratios and packing heights. However referring to equation 1.8, if the requirement for the air-stripping column in a remedial strategy is to remove substances to very low levels, packing heights will need to be set high, especially if compounds such as MTBE were present. Note that the remedial targets for MTBE and benzene were generally not met throughout the experimental trials.

Based upon limited data, the present experimental trials suggested that stainless steel structured packing could achieve higher removal efficiencies than random packing. This was particularly relevant to benzene compounds, when comparing the fuel oil results to studies such as those conducted by Stover and Kincannon (1983). Further tests should be carried out on the structured packing. This may confirm whether the material should be implemented as part of an optimised remedial strategy.

If MTBE was detected in contaminated groundwater, air-stripping technology would be applied differently than if it were not present. That is, an optimised remediation strategy if MTBE was present would have to be run at higher air-to-water ratios than if only volatile compounds such as benzene were present. This in-turn would have economic consequences to the proposed remediation strategy.

The findings of the experimental trials were not conclusive as to whether F400 or F600 should be implemented in an optimised remediation strategy designed to remove MTBE and benzene simultaneously from groundwater. Generally the adsorptive capacities of F400 and F600 were similar when the influent concentrations were comparable. It can be noted however that the highest adsorptive capacity achieved throughout the tests (for both benzene and MTBE) was by F400 GAC. This contradicts what was suggested in literature in which F600 was cited as having a much higher adsorptive capacity for MTBE. For example Sutherland *et al* (2004) suggested that for all groundwaters tested in their study, F600 carbon had significantly greater capacity for MTBE than F400 by a factor of 1.5 – 2. Referring to table 1.16, the highest capacity achieved by F600 carbon (20mg/g) occurred when BTEX compounds were not present in the influent. Therefore it is possible that the lower capacities experienced throughout the present study and the fact that the adsorptive capacities of F400 and F600

were similar, was caused by the competitive adsorptive effects of MTBE and BTEX compounds.

An optimised remediation strategy would rely upon maximising the time to component breakthrough. However, breakthrough data could not be relied upon throughout the experimental trials due to the fluctuating influent concentration. Relating the relative capacity of GAC cited in literature and the present study to an optimised remediation strategy is difficult due to the fact that at higher influent concentrations, higher capacities can be achieved. Therefore the provision of an optimised remediation strategy may come down to the contaminant levels within the groundwater. When MTBE and benzene are both present within contaminated groundwater the results of the experimental trials suggest that there is limited difference between the implementation of F400 and F600 GAC. If this is the case then the optimised remedial strategy should be based upon cheapest GAC option.

Literature suggested that the adsorptive capacity of F400 and F600 GAC was less than that of alternative adsorbents. These findings were also substantiated with the findings of the fuel oil experimental trials. It is therefore possible that if alternative adsorbents such as Ambersorb 563 gain regulatory clearance for use in the water industry, they could be implemented as part of an optimised remedial strategy. Note also that literature suggested that the adsorptive capacity of alternative adsorbents were not as affected as F400 GAC in multi-solute systems.

The competitive adsorption between compounds is likely to have impact upon the optimised remediation strategy for the remediation of contaminated groundwaters. This not only applies to BTEX and MTBE, but for TOC and BOM also. The performance of GAC can be increased if the concentrations of TOC and NOM can be reduced. Hooper *et al* (1996) suggested that coagulation can be applied before GAC columns to reduce TOC and NOM concentrations, therefore effective pre-treatment should be considered in an optimised remediation strategy.

Section 5.3 of the discussion chapter relates the performance of the fuel oil experimental trials to AOPs. AOPs are cited within literature as an alternative to air-stripping and adsorption technologies in the post-abstraction remediation of contaminated groundwater. It is evident that even at higher influent

concentrations of MTBE and benzene, AOP technology including ozone, UV-ozone, ozone-peroxide and FR can lead to higher removal efficiencies than air-stripping and adsorption technologies. In some instances, removal efficiencies of 99.9% were cited, suggesting a suitable optimisation strategy. However, in the application of the post-abstraction remediation of contaminated groundwater for immediate potable supply, the formation of harmful by-products outweighs the benefits of greater removal efficiencies. The removal of the by-products would require a further remediation step.

It was an aim of the fuel oil project to recommend areas of further investigation, with respect to the optimised removal of MTBE and BTEX compounds simultaneously from contaminated groundwater. Both the air-stripping and adsorption technologies implemented throughout the experimental trials generally did not achieve the remediation targets.

Certainly the implementation of the structured packing suggested higher removal efficiencies than tradition random packing and should therefore be investigated further. Experiments using the structured packing should include separate MTBE and BTEX experiments. This will further aid the comparison between random and structured packing. Experimental trials should utilise air-to-water ratios greater than those implemented in the present study (for example 100:1) in an effort to improve the removal of MTBE.

The results of the present study suggested a contradiction with respect to similar trials cited within literature. In order to fully investigate the influence of competitive adsorption, further trials should be carried out on F400 and F600 GAC. If possible, alternative adsorbents should also be tested and compared against the capacities of F400 and F600 GAC.

Given that the capacity of GAC is dependent on the influent concentration, if the influent concentration can be controlled more effectively using a batch system, time to component breakthrough could be investigated at different adsorbate loading rates. These results could then be transposed more easily into an optimised remediation strategy.

Experimental trials should also be carried out on AOPs, utilising GAC as a possible polishing step for the harmful by-products.

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APPENDIX A.

Table A1: Fuel Composition of Unleaded Gasoline 95.

The following information was provided by a UK Oil Company.

Sample was amalgamation of several samples takes in Mar 2001.

Detailed GC Composition:

PEAK	COMPOUND	WEIGHT%	VOLUME%
1	Propene	0.00	0.01
2	Propane	0.15	0.22
3	Isobutane	2.16	2.83
4	Isobutene + But-1-ene	0.26	0.32
5	Unknown Peak	0.00	0.00
6	n-Butane	5.08	6.38
7	tBut-2-ene	0.34	0.42
8	2,2-Dimethylpropane	0.03	0.03
9	cBut-2-ene	0.24	0.28
10	3-Methylbut-1-ene	0.07	0.08
11	Isopentane	9.94	11.68
12	Pent-1-ene	0.22	0.25
13	2-Methylbut-1-ene	0.42	0.47
14	n-Pentane	3.12	3.63
15	2-Methyl-1,3-butadiene	0.03	0.03
16	tPent-2-ene	0.72	0.81
17	3,3-Dimethylbut-1-ene	0.01	0.01
18	cPent-2-ene	0.36	0.40
19	2-Methylbut-2-ene	0.96	1.06
20	t1,3-Pentadiene	0.02	0.02
21	c1,3-Pentadiene	0.03	0.03
22	2,2-Dimethylbutane	2.32	2.60
23	Cyclopentene	0.18	0.17
24	4-Methylpent-1-ene	0.04	0.04
25	3-Methylpent-1-ene	0.06	0.07
26	Cyclopentane	0.55	0.54
27	2,3-Dimethylbutane	1.27	1.39
28	MTBE	0.61	0.60
29	4-Methyl-cpent-2-ene	0.04	0.04
30	2-Methylpentane	4.00	4.45
31	4-Methyl-tpent-2-ene	0.12	0.13
32	3-Methylpentane	2.46	2.70
33	2-Methylpent-1-ene	0.18	0.19
34	Hex-1-ene	0.09	0.09
35	n-Hexane	2.09	2.31
36	c+tHex-3-ene	0.16	0.17
37	tHex-2-ene	0.23	0.25
38	2-Methylpent-2-ene	0.36	0.38
39	3-Methyl-cpent-2-ene	0.20	0.21
40	cHex-2-ene	0.12	0.13
41	3-Methyl-tpent-2-ene	0.26	0.27
42	Methylcyclopentane	1.68	1.63
43	2,4-Dimethylpentane	0.59	0.64
44	Unknown Peak	0.01	0.01

PEAK	COMPOUND	WEIGHT%	VOLUME%
45	2,3,3-Trimethylbut-1-ene	0.03	0.03
46	2,2,3-Trimethylbutane	0.01	0.01
47	Benzene + 1-Methylcyclopentene	1.16	0.96
48	2,4-Dimethylpent-1-ene	0.01	0.01
49	3,3-Dimethylpentane	0.12	0.13
50	Cyclohexane	1.15	1.07
51	2,4-Dimethylpent-2-ene	0.01	0.02
52	5-Methylhex-1-ene	0.04	0.04
53	2-Methyl-thex-3-ene	0.01	0.01
54	4-Methyl-c/thex-2-ene	0.06	0.06
55	2-Methylhexane + 2,3-DimeC5	2.08	2.21
56	1,1-Dimethylcyclopentane	0.05	0.05
57	Cyclohexene	0.28	0.25
58	3-Methylhexane	1.42	1.51
59	3,4-Dimethyl-cpent-2-ene	0.02	0.02
60	c1,3-Dimethylcyclopentane	0.20	0.20
61	t1,3-Dimethylcyclopentane	0.18	0.17
62	t1,2-Dimethylcyclopentane	0.33	0.32
63	Isooctane	3.11	3.27
64	Hept-1-ene	0.03	0.03
65	3-Methyl-chex-3-ene	0.03	0.03
66	C7 Olefin	0.05	0.05
67	tHept-3-ene	0.11	0.12
68	n-Heptane	0.95	1.01
69	cHept-3-ene	0.07	0.07
70	2-Methylhex-2-ene	0.08	0.08
71	3-Methyl-thex-3-ene	0.06	0.06
72	tHept-2-ene	0.05	0.05
73	3-Ethylpent-2-ene	0.03	0.03
74	3-Methyl-chex-2-ene	0.04	0.05
75	cHept-2-ene	0.07	0.07
76	2,3-Dimethylpent-2-ene	0.08	0.08
77	Methylcyclohexane	0.60	0.57
78	1,1,3-Trimethylcyclopentane	0.04	0.04
79	2,2-Dimethylhexane	0.03	0.03
80	Ethylcyclopentane	0.11	0.10
81	2,5-Dimethylhexane	0.41	0.43
82	2,4-Dimethylhexane	0.45	0.47
83	1,t2,c4-Trimethylcyclopentane	0.07	0.06
84	Unknown Peak	0.03	0.03
85	Unknown Peak	0.04	0.04
86	1,t2,c3-Trimethylcyclopentane	0.03	0.03
87	2,3,4-Trimethylpentane	1.18	1.25
88	Toluene + 2,3,3-TrimeC5	13.52	11.35
89	2-Methyl-thept-3-ene	0.02	0.02
90	2,3-Dimethylhexane	0.37	0.37
91	2,5-Dimethylhex-2-ene	0.08	0.08
92	2-Methylheptane	0.31	0.32
93	4-Methylheptane	0.13	0.14
94	c1,3-Dimethylcyclohexane	0.02	0.02

PEAK	COMPOUND	WEIGHT%	VOLUME%
95	3-Methylheptane	0.53	0.54
96	1,c2,t3-Trimethylcyclopentane	0.17	0.16
97	t1,4-Dimethylcyclohexane	0.10	0.09
98	2,2,5-Trimethylhexane	0.20	0.20
99	c1,3-Ethylmethylcyclopentane	0.03	0.03
100	t1,3-Ethylmethylcyclopentane	0.02	0.02
101	2,2,4-Trimethylhexane	0.08	0.09
102	n-Octane	0.40	0.41
103	2,4,4-Trimethylhexane	0.01	0.01
104	2,3,5-Trimethylhexane	0.02	0.02
105	Unknown Peak	0.01	0.01
106	2,2-Dimethylheptane	0.02	0.02
107	2,4-Dimethylheptane	0.08	0.09
108	n-Propylcyclopentane	0.02	0.02
109	2,6-Dimethylheptane	0.01	0.01
110	1,1,3-Trimethylcyclohexane	0.05	0.04
111	Ethylbenzene	2.45	2.06
112	Unknown Peak	0.02	0.02
113	m-Xylene	6.05	5.11
114	p-Xylene	2.57	2.17
115	Unknown Peak	0.01	0.01
116	2,3-Dimethylheptane	0.09	0.09
117	3,4-Dimethylheptane	0.11	0.11
118	1,t2,c4-Trimethylcyclohexane	0.02	0.02
119	3-Methyloctane	0.15	0.15
120	o-Xylene	3.21	2.65
121	Unknown Peak	0.02	0.02
122	Isobutylcyclopentane	0.14	0.14
123	n-Nonane	0.02	0.02
124	Isopropylbenzene	0.14	0.12
125	Unknown Peak	0.03	0.03
126	3,3-Dimethyloctane	0.02	0.02
127	n-Propylbenzene	0.52	0.43
128	m-Ethyltoluene	1.75	1.47
129	p-Ethyltoluene	0.75	0.64
130	1,3,5-Trimethylbenzene	0.80	0.68
131	Unknown Peak	0.02	0.01
132	4-Methylnonane	0.05	0.05
133	o-Ethyltoluene	0.74	0.61
134	2-Methylnonane	0.07	0.07
135	3-Methylnonane	0.01	0.01
136	1,2,4-Trimethylbenzene	2.60	2.16
137	Isobutylbenzene	0.01	0.01
138	s-Butylbenzene	0.01	0.01
139	n-Decane	0.07	0.07
140	1,2,3-Trimethylbenzene	0.53	0.43
141	m-Isopropyltoluene	0.05	0.04
142	Unknown Peak	0.04	0.03
143	Indan	0.27	0.20
144	C11 Alkane	0.04	0.04

PEAK	COMPOUND	WEIGHT%	VOLUME%
145	1,3-Diethylbenzene	0.14	0.12
146	m-n-Propyltoluene	0.27	0.23
147	p-n-Propyltoluene + 1,4-Dietbz	0.08	0.07
148	n-Butylbenzene	0.25	0.21
149	Unknown Peak	0.01	0.01
150	1,3-Dimethyl-5-ethylbenzene	0.07	0.06
151	1,2-Diethylbenzene	0.10	0.08
152	o-n-Propyltoluene	0.03	0.03
153	Unknown Peak	0.03	0.02
154	4-Methyldecane	0.18	0.17
155	2-Methyldecane	0.25	0.24
156	1,4-Dimethyl-2-ethylbenzene	0.04	0.03
157	1,2-Dimethyl-4-ethylbenzene	0.41	0.34
158	1,2-Dimethyl-3-ethylbenzene	0.07	0.05
159	n-Undecane	0.05	0.05
160	1,2,4,5-Tetramethylbenzene	0.15	0.12
161	1,2,3,5-Tetramethylbenzene	0.22	0.18
162	5-Methylindan	0.18	0.13
163	4-Methylindan	0.02	0.02
164	2-Methylindan	0.19	0.15
165	s-Pentylbenzene	0.05	0.05
166	Tetralin	0.03	0.02
167	n-Pentylbenzene	0.07	0.06
168	o-n-Butyltoluene	0.02	0.02
169	Naphthalene	0.22	0.16
170	Unknown Peak	0.02	0.01
171	Dimethylindan isomer 1	0.01	0.01
172	Unknown Peak	0.02	0.02
173	Dimethylindan isomer	0.06	0.04
174	Unknown Peak	0.03	0.03
175	n-Dodecane	0.02	0.02
176	Unknown Peak	0.03	0.03
177	Unknown Peak	0.04	0.03
178	Unknown Peak	0.02	0.02
179	Unknown Peak	0.02	0.02
180	C12 Aromatic 1	0.04	0.03
181	Unknown Peak	0.02	0.01
182	Unknown Peak	0.02	0.01
183	C12 Aromatic 3	0.03	0.03
184	Unknown Peak	0.00	0.00
185	C12 Aromatic 4	0.03	0.03
186	Unknown Peak	0.01	0.01
187	C12 Aromatic	0.01	0.01
188	Unknown Peak	0.00	0.00
189	2-Methylnaphthalene	0.03	0.02
190	1-Methylnaphthalene	0.07	0.05
191	Unknown Peak	0.03	0.02
192	Unknown Peak	0.01	0.01
193	Unknown Peak	0.01	0.01

Table A1. Unleaded 95

Table A2: Composition of Unleaded Gasoline 97 (Super).

Detailed GC Composition.

PEAK	COMPOUND	WEIGHT%	VOLUME%
1	Propene	0.03	0.04
2	Isobutane	2.11	2.78
3	Isobutene + But-1-ene	0.07	0.08
4	n-Butane	6.15	7.80
5	tBut-2-ene	0.16	0.19
6	2,2-Dimethylpropane	0.03	0.04
7	cBut-2-ene	0.15	0.18
8	3-Methylbut-1-ene	0.08	0.10
9	Isopentane	13.01	15.42
10	Pent-1-ene	0.22	0.25
11	2-Methylbut-1-ene	0.50	0.56
12	n-Pentane	2.66	3.12
13	2-Methyl-1,3-butadiene	0.01	0.01
14	tPent-2-ene	0.64	0.72
15	3,3-Dimethylbut-1-ene	0.01	0.01
16	cPent-2-ene	0.33	0.37
17	2-Methylbut-2-ene	1.04	1.15
18	t1,3-Pentadiene	0.01	0.01
19	c1,3-Pentadiene	0.02	0.02
20	2,2-Dimethylbutane	0.98	1.10
21	Cyclopentene	0.31	0.30
22	4-Methylpent-1-ene	0.03	0.04
23	3-Methylpent-1-ene	0.06	0.06
24	Cyclopentane	0.40	0.39
25	2,3-Dimethylbutane	0.82	0.91
26	MTBE	1.10	1.09
27	4-Methyl-cpent-2-ene	0.04	0.04
28	2-Methylpentane	2.88	3.24
29	4-Methyl-tpent-2-ene	0.11	0.12
30	3-Methylpentane	1.88	2.08
31	2-Methylpent-1-ene	0.18	0.20
32	Hex-1-ene	0.08	0.09
33	n-Hexane	1.76	1.96
34	c+tHex-3-ene	0.16	0.17
35	tHex-2-ene	0.23	0.25
36	2-Methylpent-2-ene	0.36	0.39
37	3-Methyl-cpent-2-ene	0.21	0.23
38	cHex-2-ene	0.13	0.14
39	3-Methyl-tpent-2-ene	0.29	0.30
40	Methylcyclopentane	1.23	1.20
41	Unknown Peak	0.02	0.02
42	2,4-Dimethylpentane	0.37	0.40
43	2,3,3-Trimethylbut-1-ene	0.02	0.02
44	Benzene + 1-Methylcyclopentene	1.18	0.99
45	2,4-Dimethylpent-1-ene	0.01	0.01
46	3,3-Dimethylpentane	0.11	0.12
47	Cyclohexane	0.42	0.40

PEAK	COMPOUND	WEIGHT%	VOLUME%
48	2,4-Dimethylpent-2-ene	0.05	0.05
49	5-Methylhex-1-ene	0.03	0.04
50	2-Methyl-thex-3-ene	0.01	0.01
51	4-Methyl-c/thex-2-ene	0.09	0.10
52	2-Methylhexane + 2,3-DimeC5	1.65	1.76
53	1,1-Dimethylcyclopentane	0.03	0.03
54	Cyclohexene	0.03	0.02
55	3-Methylhexane	1.35	1.44
56	3,4-Dimethyl-cpent-2-ene	0.04	0.04
57	c1,3-Dimethylcyclopentane	0.16	0.16
58	t1,3-Dimethylcyclopentane	0.14	0.14
59	t1,2-Dimethylcyclopentane	0.29	0.28
60	Isooctane	0.99	1.05
61	Hept-1-ene	0.02	0.02
62	3-Methyl-chex-3-ene	0.05	0.05
63	C7 Olefin	0.07	0.07
64	tHept-3-ene	0.15	0.16
65	n-Heptane	0.97	1.04
66	cHept-3-ene	0.10	0.10
67	2-Methylhex-2-ene	0.13	0.14
68	3-Methyl-thex-3-ene	0.09	0.10
69	tHept-2-ene	0.07	0.08
70	3-Ethylpent-2-ene	0.04	0.04
71	3-Methyl-chex-2-ene	0.05	0.05
72	cHept-2-ene	0.10	0.10
73	2,3-Dimethylpent-2-ene	0.17	0.17
74	Methylcyclohexane	0.34	0.33
75	1,1,3-Trimethylcyclopentane	0.03	0.03
76	2,2-Dimethylhexane	0.05	0.05
77	Ethylcyclopentane	0.09	0.09
78	2,5-Dimethylhexane	0.32	0.34
79	2,4-Dimethylhexane	0.30	0.31
80	Unknown Peak	0.06	0.06
81	1,t2,c4-Trimethylcyclopentane	0.05	0.05
82	1,t2,c3-Trimethylcyclopentane	0.07	0.07
83	2,3,4-Trimethylpentane	0.50	0.53
84	Toluene + 2,3,3-TrimeC5	14.81	12.55
85	1,1,2-Trimethylcyclopentane	0.03	0.03
86	2-Methyl-thept-3-ene	0.01	0.01
87	2,3-Dimethylhexane	0.22	0.23
88	2,5-Dimethylhex-2-ene	0.10	0.10
89	2-Methylheptane	0.44	0.46
90	4-Methylheptane	0.20	0.21
91	c1,3-Dimethylcyclohexane	0.03	0.03
92	3-Methylheptane	0.59	0.61
93	1,c2,t3-Trimethylcyclopentane	0.17	0.16
94	t1,4-Dimethylcyclohexane	0.03	0.03
95	2,2,5-Trimethylhexane	0.15	0.15
96	c1,3-Ethylmethylcyclopentane	0.04	0.03
97	t1,3-Ethylmethylcyclopentane	0.02	0.02

PEAK	COMPOUND	WEIGHT%	VOLUME%
98	t1,2-Ethylmethylcyclopentane	0.01	0.01
99	2,2,4-Trimethylhexane	0.01	0.01
100	t1,2-Dimethylcyclohexane	0.01	0.01
101	1,c2,c3-Trimethylcyclopentane	0.08	0.07
102	n-Octane	0.44	0.46
103	tOct-2-ene	0.02	0.03
104	2,4,4-Trimethylhexane	0.04	0.04
105	Isopropylcyclopentane	0.01	0.01
106	2,3,5-Trimethylhexane	0.01	0.01
107	2,2-Dimethylheptane	0.02	0.02
108	2,4-Dimethylheptane	0.03	0.03
109	n-Propylcyclopentane	0.01	0.01
110	1,1,3-Trimethylcyclohexane	0.05	0.04
111	Ethylbenzene	2.69	2.28
112	m-Xylene	5.85	4.98
113	p-Xylene	2.53	2.15
114	2,3-Dimethylheptane	0.05	0.05
115	3,4-Dimethylheptane	0.06	0.06
116	3-Methyloctane	0.11	0.11
117	o-Xylene	3.09	2.58
118	Isobutylcyclopentane	0.04	0.04
119	Isopropylbenzene	0.24	0.20
120	n-Propylbenzene	1.01	0.86
121	m-Ethyltoluene	3.17	2.70
122	p-Ethyltoluene	1.40	1.19
123	1,3,5-Trimethylbenzene	1.42	1.20
124	o-Ethyltoluene	1.12	0.94
125	2-Methylnonane	0.01	0.01
126	1,2,4-Trimethylbenzene	4.18	3.50
127	Isobutylbenzene	0.05	0.04
128	s-Butylbenzene	0.05	0.04
129	1,2,3-Trimethylbenzene	0.73	0.60
130	m-Isopropyltoluene	0.10	0.08
131	Unknown Peak	0.02	0.01
132	Indan	0.26	0.20
133	C11 Alkane	0.02	0.02
134	1,3-Diethylbenzene	0.13	0.11
135	m-n-Propyltoluene	0.37	0.32
136	p-n-Propyltoluene + 1,4-Dietbz	0.26	0.22
137	n-Butylbenzene	0.35	0.30
138	1,3-Dimethyl-5-ethylbenzene	0.01	0.01
139	1,2-Diethylbenzene	0.10	0.08
140	o-n-Propyltoluene	0.08	0.07
141	4-Methyldecane	0.20	0.19
142	2-Methyldecane	0.18	0.18
143	1,2-Dimethyl-4-ethylbenzene	0.33	0.28
144	1,2-Dimethyl-3-ethylbenzene	0.06	0.05
145	1,2,4,5-Tetramethylbenzene	0.15	0.13
146	1,2,3,5-Tetramethylbenzene	0.21	0.18
147	5-Methylindan	0.06	0.05

PEAK	COMPOUND	WEIGHT%	VOLUME%
148	2-Methylindan	0.05	0.04
149	s-Pentylbenzene	0.05	0.04
150	Naphthalene	0.19	0.15
151	Unknown Peak	0.02	0.02
152	C12 Aromatic 3	0.01	0.01
153	2-Methylnaphthalene	0.01	0.01
154	1-Methylnaphthalene	0.08	0.06
155	Unknown Peak	0.04	0.03
156	Unknown Peak	0.01	0.01

Table A2. Unleaded 97.

APPENDIX B.

RSSCT Pre-Test Results.

The following graphs detail the results from the RSSCT Pre-Test

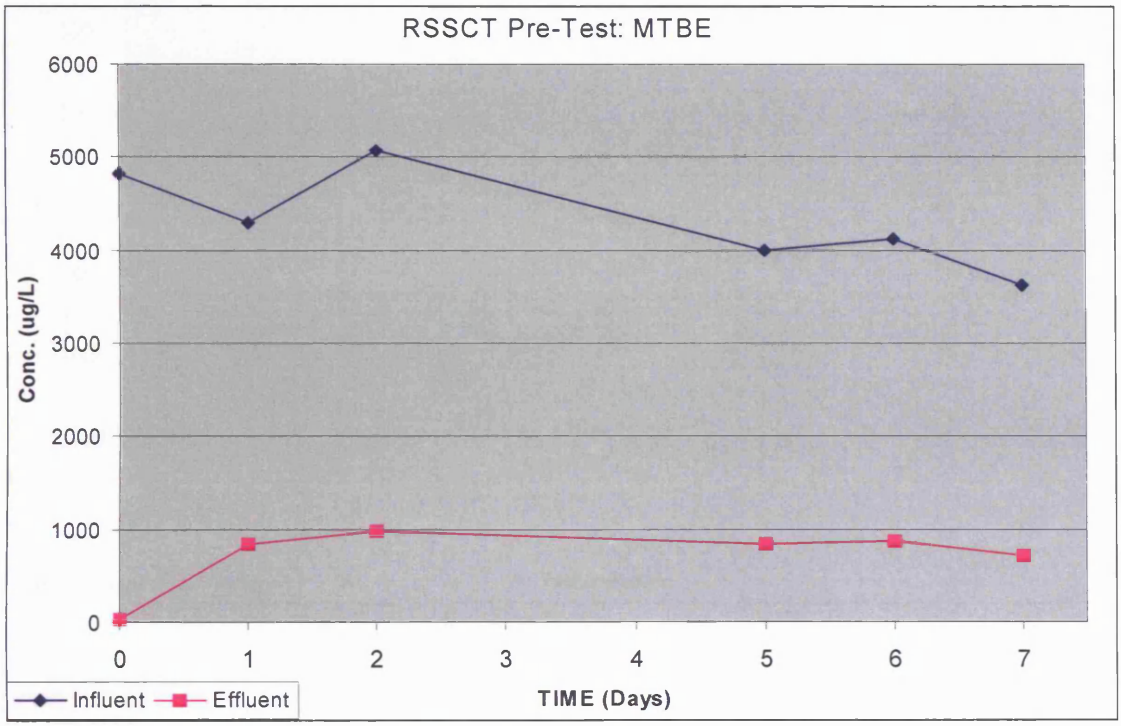

Figure A1: RSSCT Pre-Test for MTBE.

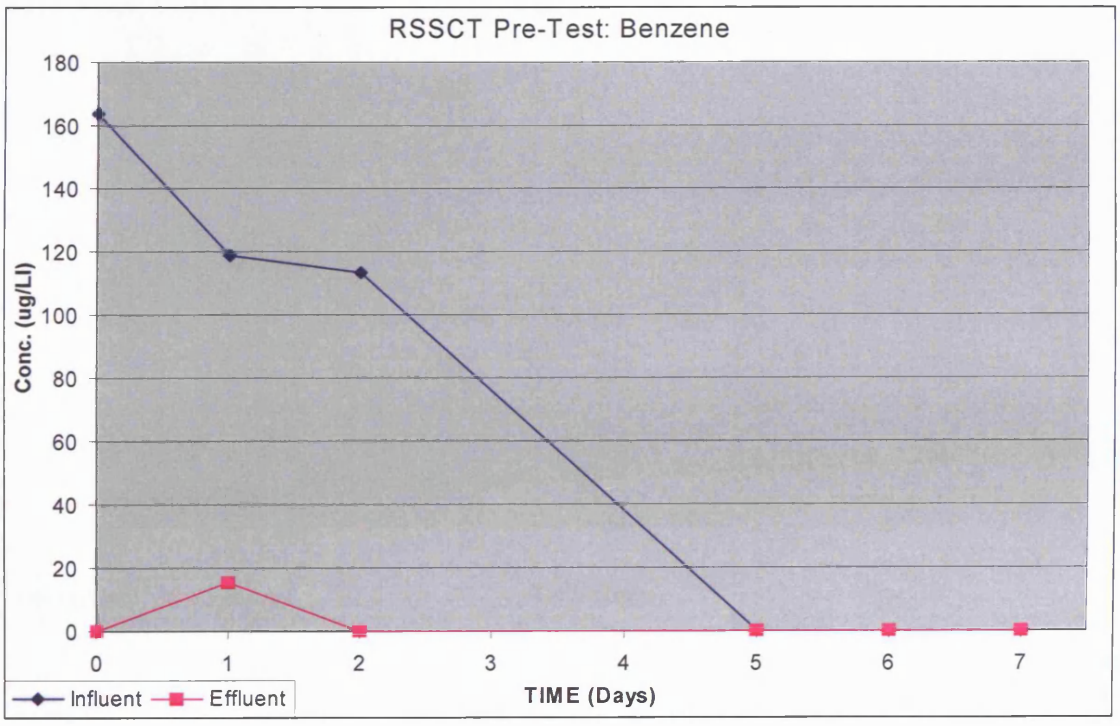

Figure A2: RSSCT Pre-Test for Benzene.

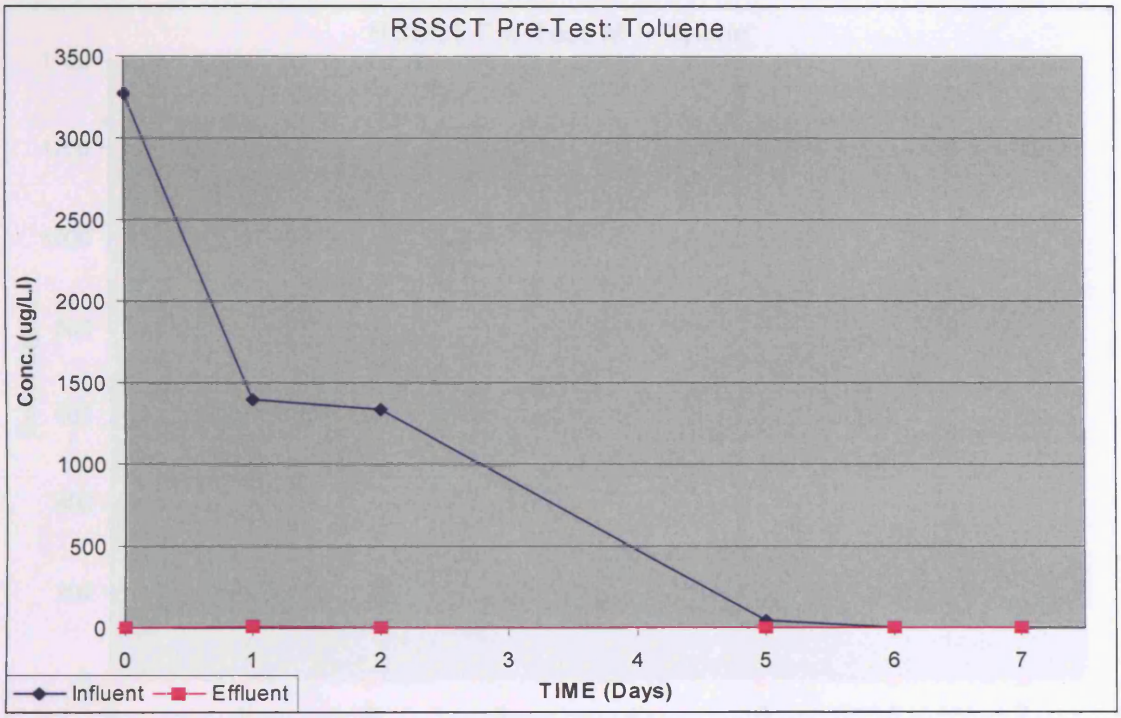

Figure A3: RSSCT Pre-Test for Toluene.

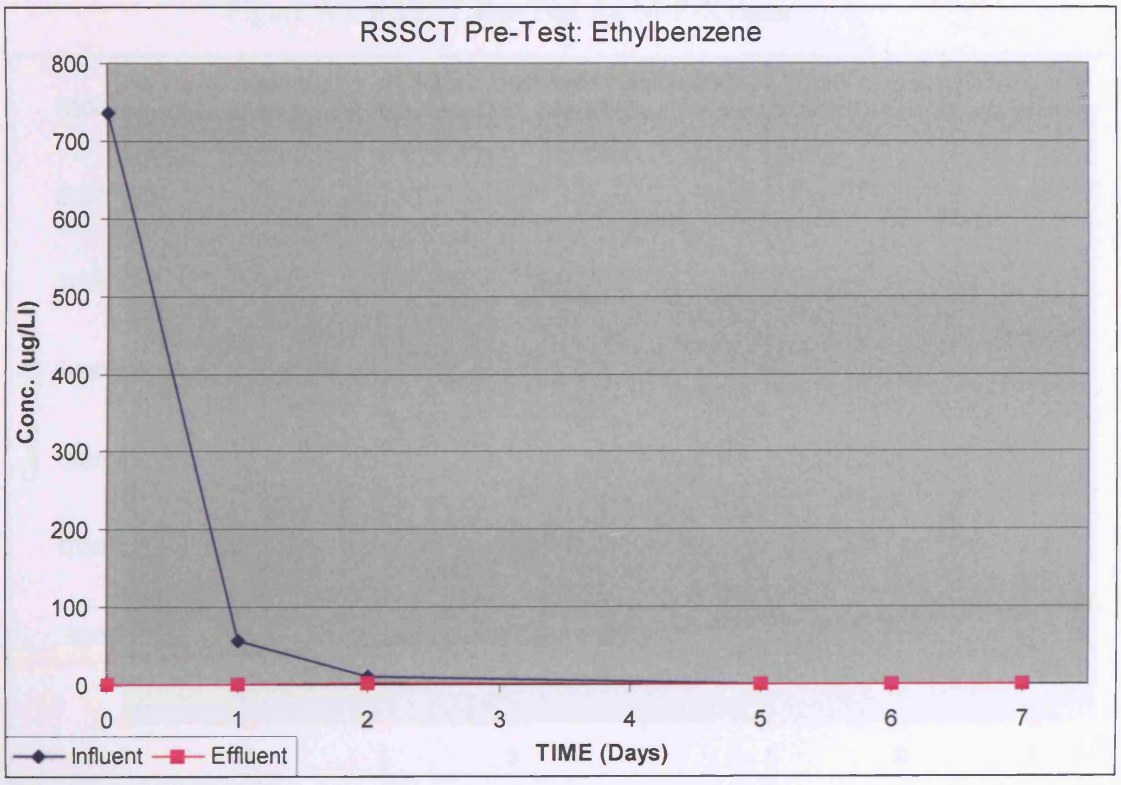

Figure A4: RSSCT Pre-Test for Ethylbenzene.

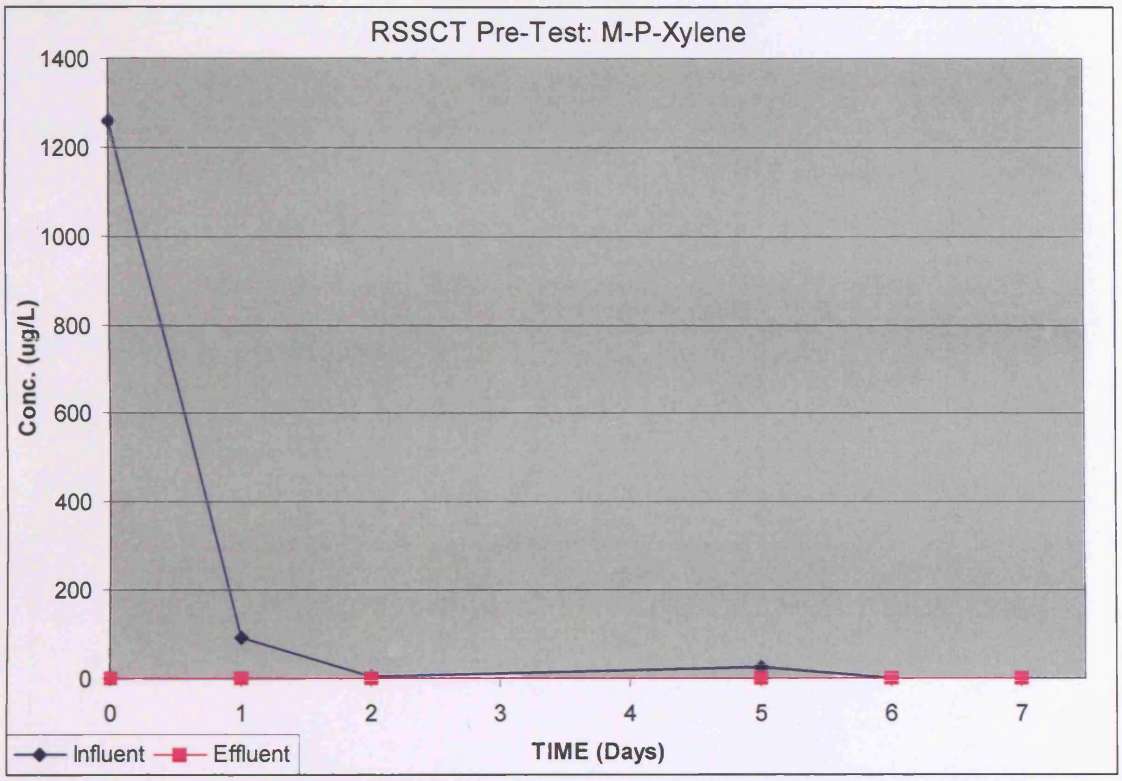

Figure A5: RSSCT Pre-Test for M-P-Xylene.

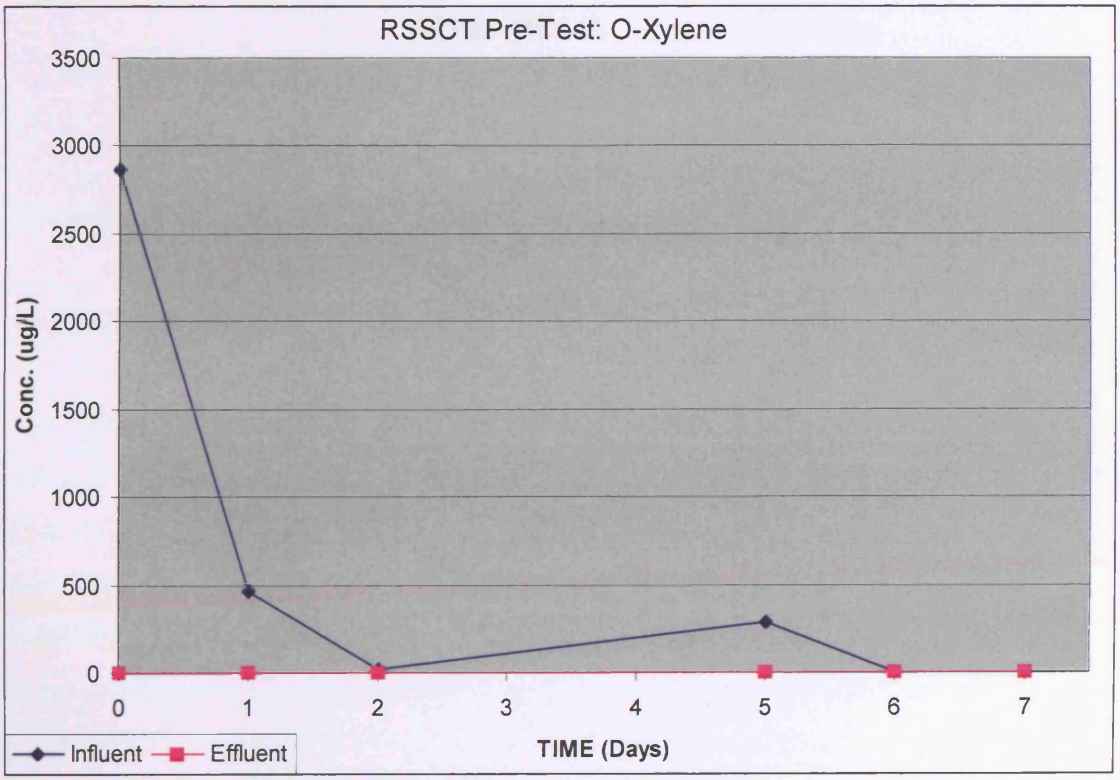

Figure A6: RSSCT Pre-Test for O-Xylene.

APPENDIX C.

GC-MS Chromatograms showing Disinfection by Product Interference.

Referring to figure A7 it can be seen that the peak shape for toluene was irregular. This irregularity was characterised by a 'hump' and trailing peak within the chromatogram, where the end of the peak was indistinguishable with the base line. As a result a level of uncertainty was experienced when integrating the peak area for toluene. For this reason the results for toluene were not considered to be accurate. Note that the dates detailed on all the chromatograms throughout this section are inaccurate. This was caused by a fault in the PC software used to run the GC-MS.

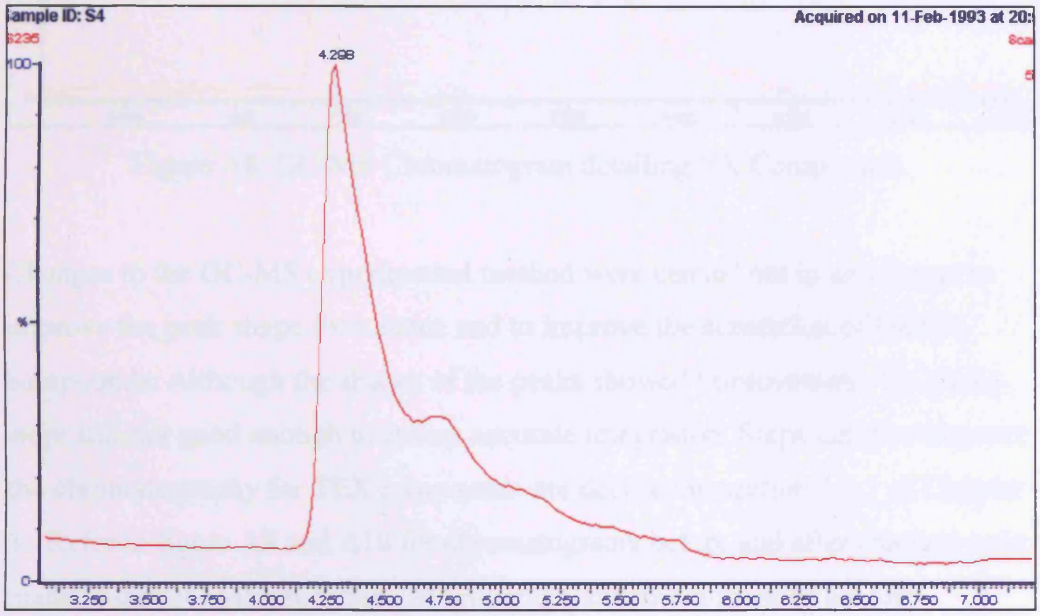

Figure A7 GC-MS Chromatogram detailing Toluene.

Referring to table 1.5 of Chapter 1 it can be seen that the physical and chemical nature of ethylbenzene and m-p-o-xylene (EX) compounds are very similar. EX compounds have identical relative molecular masses and as a result have similar solubilities and volatilities. Since volatility dictates the retention time of a compound within a GC column, it follows that EX compounds elute at similar times. Ethylbenzene is the first compound to elute, closely followed by m-p-xylene and finally o-xylene. Note that m-xylene and o-xylene elute at exactly the same time, hence quantification of each individual compound was not possible. Figure A8 illustrates a common EX peak found throughout the experimental period.

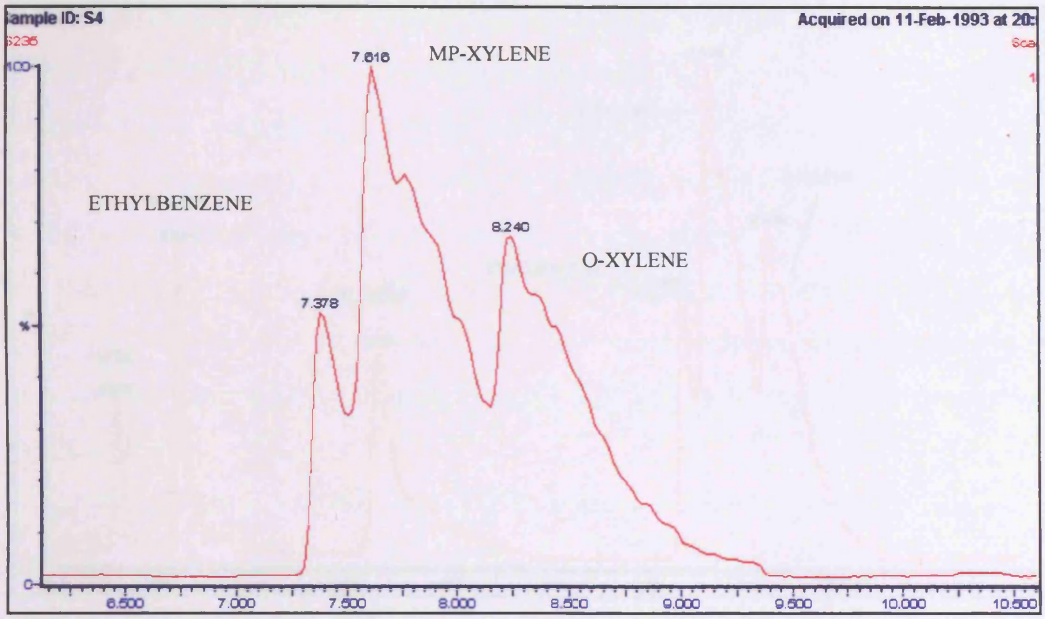

Figure A8. GC-MS Chromatogram detailing EX Compounds.

Changes to the GC-MS experimental method were carried out in an attempt to improve the peak shape for toluene and to improve the separation of the EX compounds. Although the shapes of the peaks showed improvement, the peaks were still not good enough to ensure accurate integration. Steps taken to improve the chromatography for TEX compounds are detailed in section 3.1.1 of Chapter 3. Refer to figure A9 and A10 for chromatograms before and after changes were made to the GC-MS procedure. MTBE and benzene compounds are also detailed.

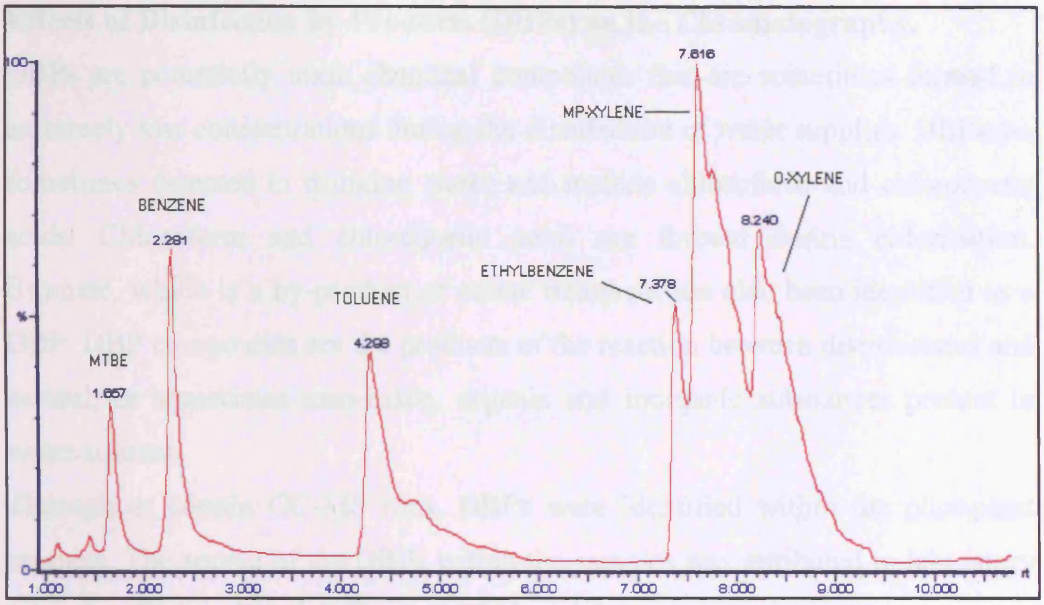

Figure A9. GC-MS Chromatogram detailing MTBE and BTEX Compounds, before Method Change.

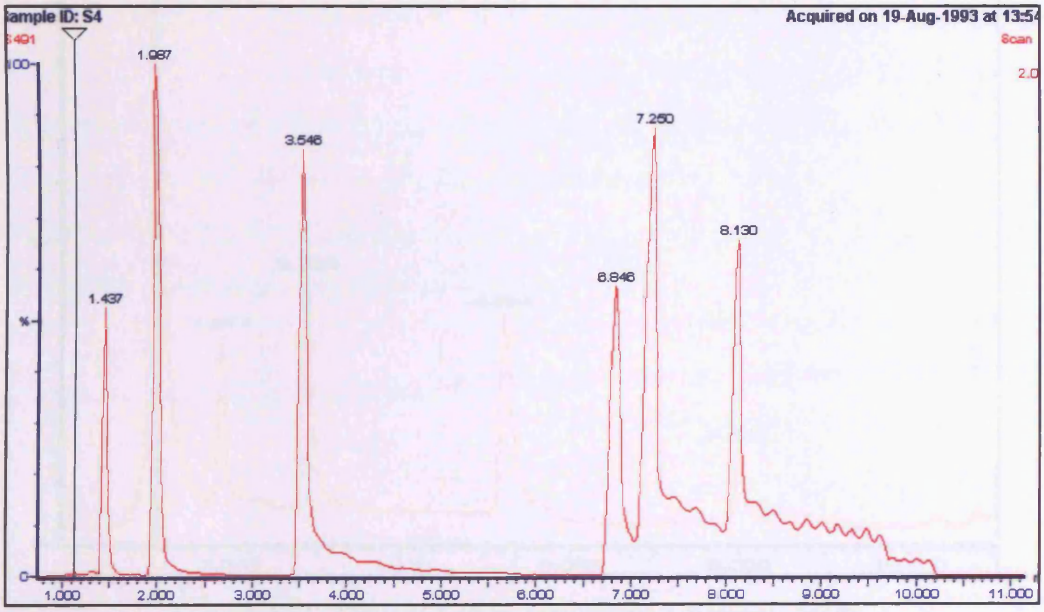

Figure A10. GC-MS Chromatogram detailing MTBE and BTEX Compounds, after Method Change.

Effects of Disinfection by-Products (DBPs) on the Chromatography.

DBPs are potentially toxic chemical compounds that are sometimes formed in extremely low concentrations during the disinfection of water supplies. DBPs are sometimes detected in drinking water and include chloroform and chloroacetic acids. Chloroform and chloroacetic acids are formed during chlorination. Bromate, which is a by-product of ozone treatment has also been identified as a DBP. DBP compounds are the products of the reaction between disinfectants and natural, or sometimes man-made, organic and inorganic substances present in water sources.

Throughout certain GC-MS runs, DBPs were identified within the pilot-plant samples. The source of the DBPs within the samples was attributed to laboratory tap water. Figure A11 details a typical blank laboratory water sample.

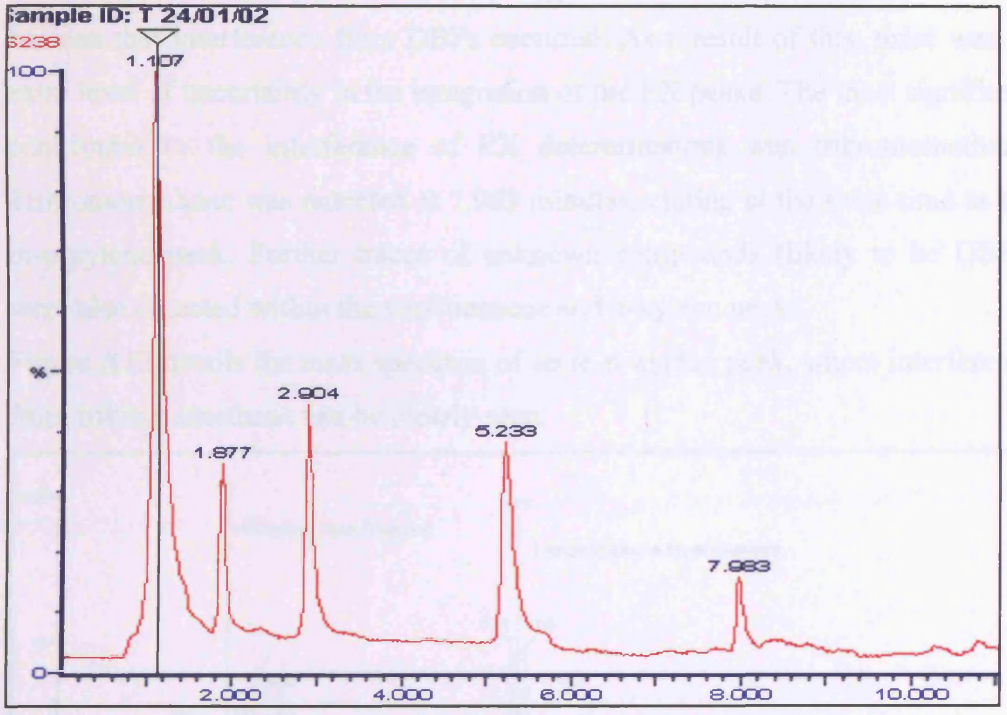

Figure A11. Typical Laboratory Blank Chromatogram.

Table A3 details the DPSs found in the laboratory water during run 7, and their retention times.

Compound	Retention Time (mins)
2,2,2-Trifluoroethanol	1.107
Chloroform	1.877
Bromodichloromethane	2.040
Dibromochloromethane	5.233
Tribromomethane	7.983

Table A3. DBPs found in Laboratory Supply Water.

Cases where DBPs were present in pilot-plant samples led to added complications in the determination and quantification of EX compounds. In reviewing the integration of EX peaks on specific GC-MS chromatograms it can be seen that interference from DBPs occurred. As a result of this, there was an extra level of uncertainty in the integration of the EX peaks. The most significant contributor to the interference of EX determinations was tribromomethane. Tribromomethane was detected at 7.983 minutes, eluting at the same time as the m-p-xylene peak. Further traces of unknown compounds (likely to be DBPs) were also detected within the ethylbenzene and o-xylene peaks.

Figure A12 details the mass spectrum of an m-p-xylene peak, where interference from tribromomethane can be clearly seen.

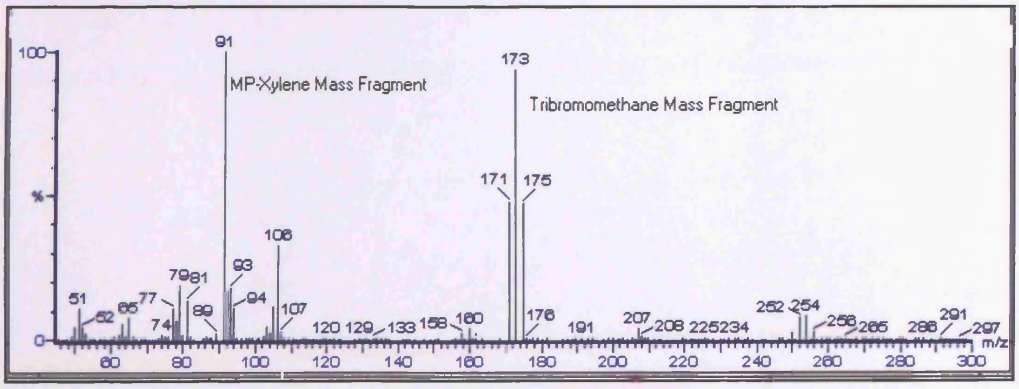

Figure A12. Mass Chromatogram of an M-P-Xylene Peak.

In conclusion it was decided that the TEX results could not be relied upon. For this reason the results and discussion section detailed MTBE and benzene compounds only. This was viewed as an acceptable change to the study due to the fact that the aim of the study was to design a remediation process for the removal of MTBE and benzene. Although TEX compounds were not presented

throughout the results chapter or used to formulate the discussion/ conclusion chapter, the compounds were added to the fuel oil concentrate throughout the entire experimental phase. Removing TEX compounds from the fuel concentrate part way through the experimental phase would have altered the make-up of the influent water. The study should therefore be referred to as the removal of MTBE and benzene from a synthetic fuel mix by air-stripping and adsorption – in the presence of TEX compounds.

APPENDIX D.

Example TEX Results.

As discussed at the beginning of Chapter 4, problems were encountered with the identification and quantification of the TEX compounds throughout the entire GC-MS analysis period. Whilst it was obvious that the compounds were present in the influent and were being removed at each stage of the remediation process, the physiochemical nature of the compounds meant that the compounds could not be quantified to any degree of satisfactory certainty. This was discussed in Appendix C.

TEX compounds were still added to the influent of the pilot-plant throughout the entire experimental period, as changing one of the main process parameters could have affected the outcome of the results.

Table A4 presents TEX results for Run 7. All values are presented in ug/L, where NDA = no data available.

TAGUCHI 7		Influent to AS	Effluent to AS	BD 25mm	BD 50mm	BD 175mm
Day 1	Toluene		17	<1	<1	NDA
	Ethlybenzene		6.7	<1	<1	NDA
	MP-Xylene		6.9	<1	<1	NDA
	O-Xylene		11	<1	<1	NDA
Day 4	Toluene	70	13	1.7	<1	NDA
	Ethlybenzene	56	6.7	1.6	<1	NDA
	MP-Xylene	52	7.3	<1	<!	NDA
	O-Xylene	56	12	1.3	<1	NDA
Day 6	Toluene	133	15	2.5	1.3	NDA
	Ethlybenzene	106	7.6	<1	<1	NDA
	MP-Xylene	102	8.5	1.5	<1	NDA
	O-Xylene	102	14	2.1	<1	NDA
Day 8	Toluene	151	9.9	4.5	1.4	NDA
	Ethlybenzene	79	3.9	1.1	<1	NDA
	MP-Xylene	84	5.1	1.3	<1	NDA
	O-Xylene	86	7.8	1.8	<1	NDA
Day 12	Toluene	148	11	4.3	1.3	NDA
	Ethlybenzene	181	5.3	1.3	<1	NDA
	MP-Xylene	150	6.1	1.7	<1	NDA
	O-Xylene	160	10	2.2	<1	NDA
Day 14	Toluene	111	31	10	3.3	NDA
	Ethlybenzene	122	15	3.5	<1	NDA
	MP-Xylene	116	17	4.5	1.5	NDA
	O-Xylene	124	27	7.2	2.5	NDA
Day 16	Toluene	127	22	4.7	2.4	NDA
	Ethlybenzene	105	14	2.6	<1	NDA
	MP-Xylene	99	14	2.1	<1	NDA
	O-Xylene	125	21	3.3	1.3	NDA
Day 19	Toluene	157	15	2.5	1.9	NDA
	Ethlybenzene	168	7.7	1.4	<1	NDA
	MP-Xylene	56	8.2	1.2	<1	NDA
	O-Xylene	89	13	1.9	<1	NDA
Day 21	Toluene	125	17	6.1	3.7	NDA
	Ethlybenzene	52	11	2.9	1.6	NDA
	MP-Xylene	38	11	2.5	1.2	NDA
	O-Xylene	114	17	4.4	2.0	NDA

Table A4. TEX Results from Run 7.

Results presented in this section were for toluene only.

Figure A13 presents influent and effluent concentrations to the air-stripper for toluene, during Taguchi run 7.

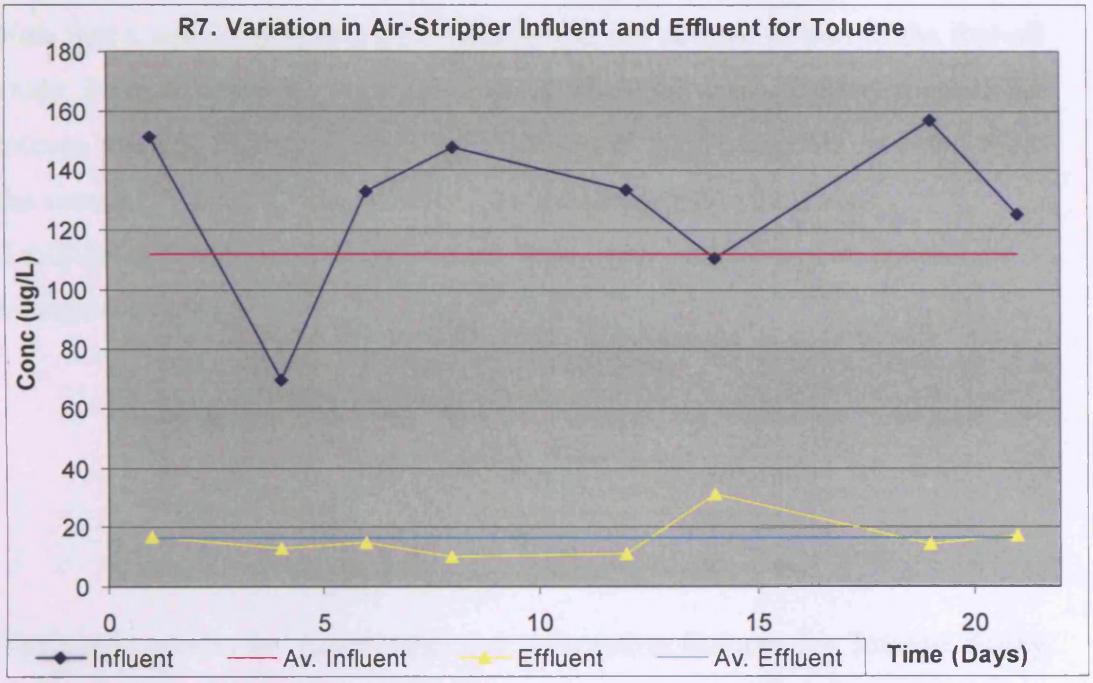

Figure A13. Graph to show Influent and Effluent Concentrations for Toluene, during Run 7.

From figure A13 it can be seen that the air-stripper is reasonably effective at removing toluene, with an approximate removal efficiency of 80%.

Figure A14 details the breakthrough curve for Toluene during Run 7.

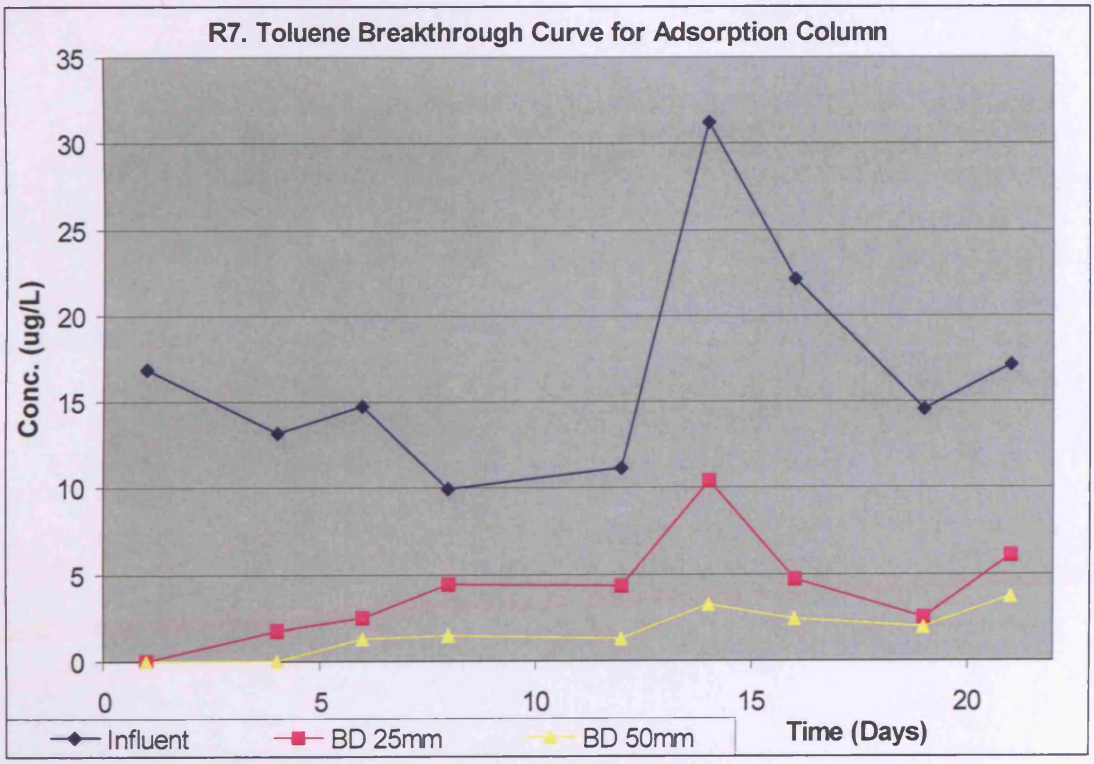

Figure A14. Adsorption Column Breakthrough Curve for Toluene, during Run 7.

Note that a remediation target for toluene was not defined as part of the fuel-oil study. From figure A14 it can be seen that the GAC was effective at removing toluene towards the beginning of the experiment. As the experiment progressed, the concentration of toluene in BD 25 and 50mm began to increase.

Table A5 details the ARE% for both the air-stripper and adsorption column for toluene during Run 7.

	ARE (%)	
Air-Stripper	87	
Adsorption Column	BD 25mm	BD 50mm
	72	90

Table A5. ARE% for Air-Stripper and Adsorption Column for Toluene during Run 7.

APPENDIX E.

Pilot-Plant Pre-Test Results.

Table A6: Pilot-Plant Pre-Test Results. NDA = No Data Available.

Note: Data for benzene was not available due to co-elution problems experienced during quantification.

Pre-Test		Influent to AS	Effluent to AS	BD 25mm	BD 50mm
Day 1	MTBE	NDA	NDA	22	19
	Toluene	NDA	NDA	2	1
	Ethylbenzene	NDA	NDA	2	1
	MP-Xylene	NDA	NDA	3	2
	O-Xylene	NDA	NDA	<1	<1
Day 4	MTBE	NDA	12	22	19
	Toluene	NDA	2	1	<1
	Ethylbenzene	NDA	1	1	1
	MP-Xylene	NDA	2	1	1
	O-Xylene	NDA	2	2	<1
Day 6	MTBE	NDA	22	19	18
	Toluene	NDA	2	1	<1
	Ethylbenzene	NDA	<1	<1	<1
	MP-Xylene	NDA	1	1	1
	O-Xylene	NDA	1	1	5
Day 8	MTBE	NDA	18	13	14
	Toluene	NDA	1	<1	<1
	Ethylbenzene	NDA	1	1	1
	MP-Xylene	NDA	2	2	2
	O-Xylene	NDA	1	1	<1
Day 11	MTBE	25	16	13	13
	Toluene	6	1	<1	<1
	Ethylbenzene	7	2	1	1
	MP-Xylene	7	2	2	2
	O-Xylene	13	<1	<1	<1
Day 13	MTBE	14	12	12	12
	Toluene	1	1	<1	<1
	Ethylbenzene	2	1	1	1
	MP-Xylene	2	2	2	2
	O-Xylene	2	1	1	2
Day 18	MTBE	17	13	NDA	NDA
	Toluene	7	1	NDA	NDA
	Ethylbenzene	6	1	NDA	NDA
	MP-Xylene	9	2	NDA	NDA
	O-Xylene	13	1	NDA	NDA

Table A6. Pilot-Plant Pre-Test Results.

Air-stripper results for MTBE during Pilot-Plant Pre-Test.

Figure A15. Graph to Show Air-Stripper for MTBE during Pilot-Plant Pre-Test.

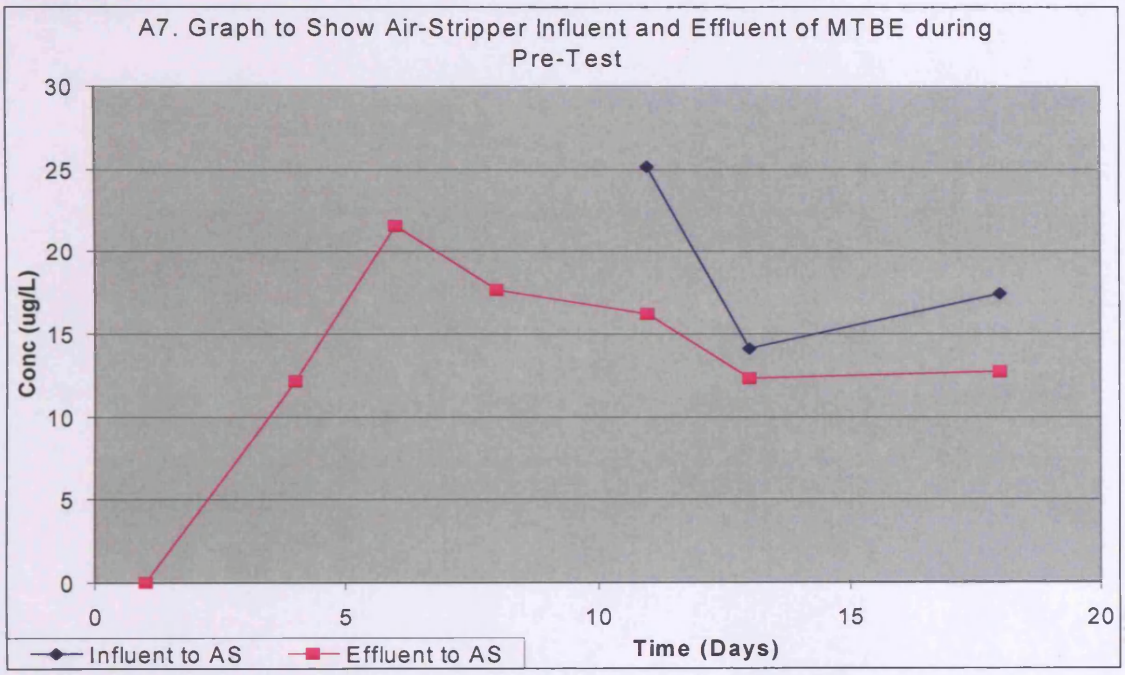

Figure A15. Graph to Show Air-Stripper for MTBE during Pilot-Plant Pre-Test.

Adsorption column results for MTBE during Pilot-Plant Pre-Test.

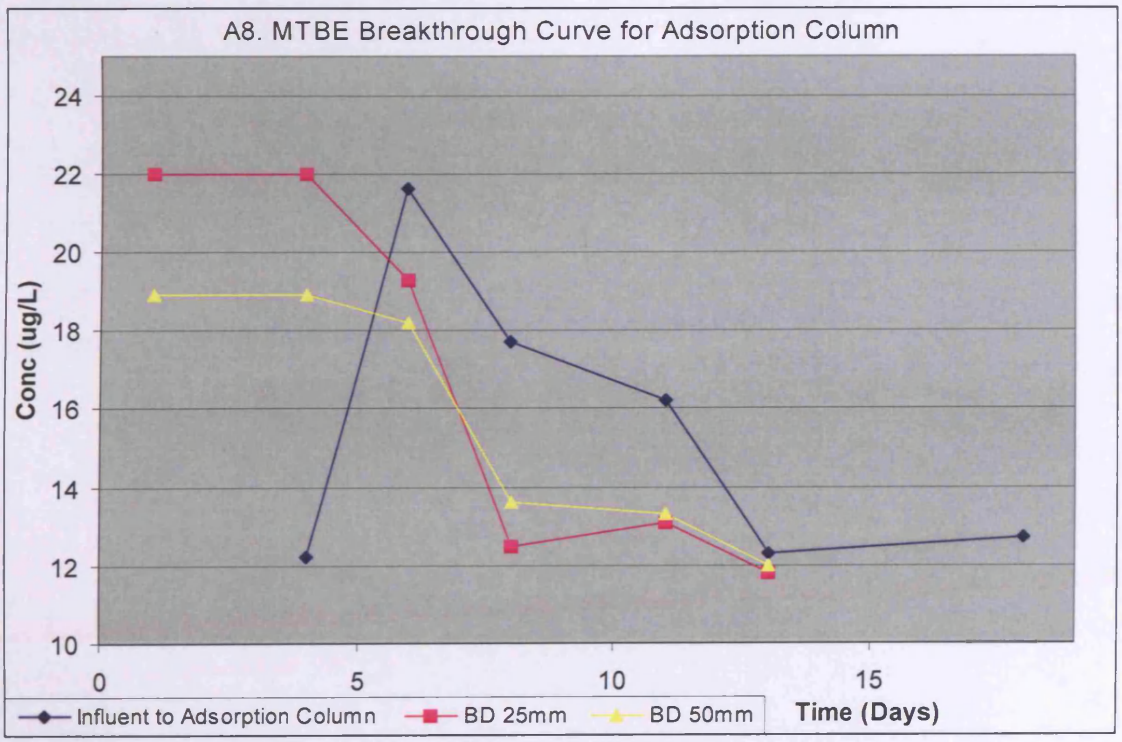

Figure A16. Adsorption Column Breakthrough Curve for MTBE, during Pre-Test.

APPENDIX F.

THAMES WATER UTILITIES

SCHEDULE 4 REPORT - WATER SUPPLY (WATER QUALITY) REGULATIONS 1989 (30(4))

WATER SUPPLY ZONE NLE16 : BLOOMSBURY Zone No. : 0016

Time Period: 01/01/1999 to 31/12/1999
Population : 30700

Parameter	Units	PCV	Concentration or value (all samples) Min	Mean	Max	No. of Samples Total	Contrav -ening	% of samples contrav -ening PCV
Colour (Pt/Co scale)	mg/l Pt/Co	20	1	2	5	10	0	0.0
Turbidity	F.t.u.	4	< 0.3	< 0.3	0.4	10	0	0.0
Odour (qualitative)		-	0	0	0	84	0	0.0
Taste (qualitative)		-	0	0	0	84	0	0.0
Odour (quantitative)		3	0	0	0	5	0	0.0
Taste (quantitative)		3	0	0	0	5	0	0.0
Temperature	degrees C	25	7.0	14.3	22.0	84	0	0.0
Hydrogen Ion	pH value	5.5 to 9.5	8.0	8.1	8.2	10	0	0.0
Sulphate as SO4	mg/l	250	54	54	54	1	0	0.0
Magnesium as Mg	mg/l	50	4.9	4.9	4.9	1	0	0.0
Sodium as Na	mg/l	150	27.8	27.8	27.8	1	0	0.0
Potassium as K	mg/l	12	5.1	5.1	5.1	1	0	0.0
Nitrate as NO3	mg/l	50	24.3	30.6	36.3	10	0	0.0
Nitrite as NO2	mg/l	0.1	< 0.010	< 0.016	0.050	36	0	0.0
Ammonium as NH4	mg/l	0.5	< 0.064	< 0.093	0.116	10	0	0.0
Oxidisability (PV) as O2	mg/l	5	1.30	1.30	1.30	1	0	0.0
Total Org. Carbon as C	mg/l	-	3.00	3.00	3.00	1	0	0.0
Surfactants	ug/l	200	36	36	36	1	0	0.0
Aluminium as Al	ug/l	200	< 14	< 14	< 14	10	0	0.0
Iron as Fe	ug/l	200	< 12	< 13	24	10	0	0.0
Manganese as Mn	ug/l	50	< 3	< 3	< 3	10	0	0.0
Copper as Cu	ug/l	3000	< 20	< 118	242	4	0	0.0
Zinc as Zn	ug/l	5000	< 18	< 18	< 18	4	0	0.0
Phosphorus as P	ug/l	2200	539	539	539	1	0	0.0
Fluoride as F	ug/l	1500	172	172	172	1	0	0.0
Silver as Ag	ug/l	10	< 1.0	< 1.0	< 1.0	1	0	0.0
Arsenic as As	ug/l	50	2	2	2	1	0	0.0
Cadmium as Cd	ug/l	5	< 0.5	< 0.5	< 0.5	1	0	0.0
Cyanide as CN	ug/l	50	< 5	< 5	< 5	1	0	0.0
Chromium as Cr	ug/l	50	< 5	< 5	< 5	1	0	0.0
Mercury as Hg	ug/l	1	< 0.05	< 0.05	< 0.05	1	0	0.0
Nickel as Ni	ug/l	50	< 4	< 4	< 4	1	0	0.0
Lead as Pb	ug/l	50	< 5	< 5	< 5	4	0	0.0
Antimony as Sb	ug/l	10	< 0.8	< 0.8	< 0.8	1	0	0.0
Selenium as Se	ug/l	10	1.1	1.1	1.1	1	0	0.0
Atrazine	ug/l	0.1	< 0.010	< 0.012	0.030	113	0	0.0
Simazine	ug/l	0.1	< 0.010	< 0.010	0.020	113	0	0.0
Chlortoluron	ug/l	0.1	< 0.020	< 0.020	< 0.020	113	0	0.0
Diuron	ug/l	0.1	< 0.020	< 0.020	< 0.020	113	0	0.0
Isoproturon	ug/l	0.1	< 0.020	< 0.021	0.070	113	0	0.0
Linuron	ug/l	0.1	< 0.020	< 0.020	< 0.020	113	0	0.0
Propazine	ug/l	0.1	< 0.020	< 0.020	< 0.020	113	0	0.0
Propyzamide	ug/l	0.1	< 0.040	< 0.040	< 0.040	113	0	0.0
Terbutryn	ug/l	0.1	< 0.030	< 0.030	< 0.030	113	0	0.0

NOTE : PCV = Prescribed Concentration or Value

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SCHEDULE 4 REPORT - WATER SUPPLY (WATER QUALITY) REGULATIONS 1989 (30(4))

WATER SUPPLY ZONE NLE16 : BLOOMSBURY Zone No. : 0016

Time Period: 01/01/1999 to 31/12/1999
Population : 30700

Parameter	Units	PCV	Concentration or value (all samples) Min	Mean	Max	No. of Samples Total	Contrav-ening	% of samples contrav-ening PCV
Prometryn	ug/l	0.1	< 0.030	< 0.030	< 0.030	113	0	0.0
Bromoxynil	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
Ioxynil	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Dicamba	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
MCPA	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
MCPB	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Mecoprop	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
2,4-D	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
Pentachlorophenol	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
Dichlorprop	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Bentazone	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Triclopyr	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Fluroxypyr	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
Picloram	ug/l	0.1	< 0.020	< 0.020	< 0.020	61	0	0.0
2,4,5-T	ug/l	0.1	< 0.010	< 0.010	< 0.010	61	0	0.0
Total Pesticides	ug/l	0.5	0.000	0.014	0.070	113	0	0.0
Benzo 3.4 pyrene	ng/l	10	< 5	< 5	< 5	4	0	0.0
Fluoranthene	ug/l	-	< 0.010	< 0.011	0.015	4	0	0.0
Benzo 1.12 perylene	ug/l	-	< 0.010	< 0.010	< 0.010	4	0	0.0
Benzo 3.4 fluoranthene	ug/l	-	< 0.010	< 0.010	< 0.010	4	0	0.0
Benzo 11.12 fluoranthene	ug/l	-	< 0.010	< 0.010	< 0.010	4	0	0.0
Indeno(1,2,3-cd)pyrene	ug/l	-	< 0.010	< 0.010	< 0.010	4	0	0.0
PAHs	ug/l	0.2	0.000	0.004	0.015	4	0	0.0
Total Coliforms	no./100ml	0	0	0	1	84	1	1.2
Faecal Coliforms	no./100ml	0	0	0	0	84	0	0.0
Colony Count 22C	no./ml	-	0	0	> 300	84	0	0.0
Colony Count 37C	no./ml	-	0	0	> 300	84	0	0.0
Residual Disinfectant	mg/l	-	0.28	0.52	0.91	84	0	0.0
Conductivity at 20C	uS/cm	1500	601	623	650	42	0	0.0
Chloride as Cl	mg/l	400	40	40	40	1	0	0.0
Calcium as Ca	mg/l	250	112	112	112	1	0	0.0
Boron as B	ug/l	2000	130	130	130	1	0	0.0
Barium as Ba	ug/l	1000	18	18	18	1	0	0.0
Tetrachloromethane	ug/l	3	< 0.1	< 0.1	< 0.1	4	0	0.0
Trichloroethene	ug/l	30	< 1.0	< 1.0	< 1.0	4	0	0.0
Tetrachloroethene	ug/l	10	< 1.0	< 1.8	4.0	4	0	0.0
Total Hardness as Ca	mg/l	-	120	120	120	1	0	0.0
Alkalinity as HCO3	mg/l	-	275	275	275	1	0	0.0
Trichloromethane	ug/l	-	3	6	9	4	0	0.0
Dichlorobromomethane	ug/l	-	4	7	9	4	0	0.0
Dibromochloromethane	ug/l	-	8	9	10	4	0	0.0
Tribromomethane	ug/l	-	2	3	5	4	0	0.0
Trihalomethanes	ug/l	100	18	24	29	4	0	0.0

NOTE : PCV = Prescribed Concentration or Value

UKJH 66

Thames Water Utilities

Schedule 4 Report - Water Supply (Water Quality) Regulations 1989 (30(4))

WATER SUPPLY ZONE	NLE16: BLOOMSBURY	**Zone No:**	0016
FOR PERIOD	01/01/1999-31/12/1999	**Population:**	30,700

Commentary on Water Quality

Very good quality but one infringement to report. This infringement was investigated in accordance with the guidelines set by the Department of Environment, Transport and the Regions (DETR).

Total coliforms detected on one occasion. Investigations at the sample location failed to show any ongoing presence of coliforms. Samples for total coliforms are collected from customers premises, when coliforms are detected the customer concerned is contacted.

The standard for total coliforms is assessed on a 95% compliance basis. Therefore, there is not an infringement of the standard in this zone.

Action taken to comply with Section 19(1)(b) Undertakings

A section 19(1)(b) Undertaking is a programme of work agreed between Thames Water and the Government. Undertakings are designed to ensure that water supplies meet the standards required in the UK Drinking Water Quality Regulations. The existence of an Undertaking for a particular parameter does not indicate that the water fails to meet the standard. The Government only accept Undertakings where they are satisfied that infringements of the standard that may occur before the work is completed do not risk public health.

Nitrite - Further refine the control of ammonia dosing to optimise monochloramine formation at Hampton, Ashford, and Coppermills water treatment works. Maintain the internal performance monitors. Increase nitrite monitoring at selected service reservoirs in order to monitor nitrite formation. On findings, review and implement any changes to current operating practices to reduce service reservoir turnover times and hence reduce nitrite formation. Report progress to the DWI at six monthly intervals.

Actions completed on Undertakings in this zone

Nitrite: Hampton, Ashford Common and, Coppermills water treatment works. The control of ammonia dosing has been optimised and operational practices have been reviewed and amended where appropriate. Work as agreed in the Undertaking was completed in December 1999.

APPENDIX G.

SEPARATION OF *METHYL TERTIARY BUTYL ETHER* (MTBE) AND FUEL OIL CONTAMINATION FROM GROUNDWATER FOR POTABLE SUPPLY.

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Abstract: New drinking water regulations to be introduced in the United Kingdom in December 2003 state a maximum permissible limit for benzene of 1.0µg/l (Short, C 2001). MTBE/ toluene/ ethylbenzene and *o/m/p* xylene do not have a specific standard. However they are readily detectable in drinking water at quite low concentrations. Cases of petrochemical and fuel oil contamination of groundwater aquifers are common. The main threat to groundwater supplies comes from leakage from above and underground storage tanks. Although *in-situ* remediation methods can remove significant amounts of the organic contamination, practical steps must be taken at potable water supply (PWS) boreholes downstream of the contamination source, to protect the supply and ensure the quality of the water. This paper outlines the on-going development of a modular post abstraction remediation system using a combination of air-stripping, granular activated carbon (GAC) and advanced oxidation to remove trace concentrations of fuel oils, with particular emphasis on the removal of MTBE. Results will be presented from initial tests using rapid column test (RCT) apparatus to test the capacity of GAC to remove a variety of fuels.

Keywords. Air-stripping, Adsorption, GAC, Advanced Oxidation, Post Abstraction Remediation.

Introduction.

The nature of the petrochemical contamination of groundwater, specifically the movement of the contamination through the sub surface environment, is governed by a number of site-specific conditions. These conditions include the type of fuel, the geology of the local area and the groundwater chemistry. Once fuel oil contamination has occurred, compounds will begin to separate according to the their chemical and physical characteristics. Compounds present in fuel oil that have low solubility, low volatility and strong adsorption characteristics will be found throughout the soil near a contaminated site. These compounds include paraffins within the range C_6 to C_{30}. High volatility compounds will be found in the soil gases (e.g. pentane, hexane, cyclopropane, cyclopentane). Soluble constituents will be found within the aquifer water itself. These include MTBE, benzene, toluene, ethylbenzene, xylene (BTEX) and other monoaromatic hydrocarbons (Kaplan *et al,* 1996*)*. The soluble fractions of fuel oil (alkylbenzenes and alkylaromatic species) and any transformation products from them are more likely to reach groundwaters than any other constituents of the contamination.

Advection, dispersion, sorption and biological/chemical degradation are the processes that most strongly influence organic solute transport in saturated groundwater environments (Roberts *et al,* 1982). Given time and under the right conditions, aquifers have the ability to restore water quality after contamination with petrochemicals through natural attenuation (Deutsch, 1997). The most significant form of natural attenuation within the subsurface environment is the action of microorganisms on the fuel oil. The use of *in-situ* remediation methods have been well documented, and include the pumping of the free-floating product, *in-situ* biodegradation, soil vapour extraction (SVE) and *in-situ* air sparging. However, even if a contamination event is detected early and *in-situ* remediation methods are implemented quickly, readily dissolvable organic contaminants such as MTBE will be transported down stream of the contaminated area. The cost of treating MTBE contaminated water with conventional post abstraction technologies such as air-stripping and GAC can be 40-80% higher than treating contaminated water with other hydrocarbons such as benzene (Keller *et al* 2000*)*. Further research into MTBE remediation to improve such performance is worthwhile.

Three post abstraction methods are being applied in this investigation: air-stripping, adsorption and advanced oxidation. The process of air-stripping involves the continuous contact of the contaminated water with large volumes of air. This process aims to remove a significant fraction of the VOCs to the air phase. The removal efficiency of the contaminants from water is governed by the Henry's Law constant of each compound and the design of the air-stripper. Additional air treatment may be required if the contaminant is present in large quantities in the air phase. In adsorption treatment, solute molecules become attached to solid surfaces under the attracting influence of surface forces (van der Waals forces). It is primarily a surface phenomenon. Granular activated carbon is the most widely used adsorbent in water treatment. Advanced oxidation processes are based on the production of free radicals (OH·) using hydrogen peroxide, ozone or via an ultraviolet source. Ultimately the series of reactions between the contaminants and the free radicals will produce carbon dioxide and water. However, incomplete oxidation of some compounds can produce by-products that are more toxic than the original reactant.

Objectives.

Conventional and novel treatment technologies will be investigated to provide a modular, rapid response post abstraction treatment system for the removal of trace fuel oil contamination from potable groundwater sources. It is envisaged that the technology developed will be easily transported to the threatened borehole water treatment works (WTW) where it will be rapidly integrated into the existing treatment system and act as a safeguard for the quality of the potable water as needed.

Materials and Methods.

Preliminary experiments were carried out on a rapid column test apparatus (RCT), to investigate the performance of GAC removal of fuel oil compounds including BTEX and MTBE. RCT experiments use fine GAC particles and small column sizes to reduce the operation time compared to that of a pilot plant, providing rapid results. The GAC is crushed until it is an appropriate size for the columns. Once added to the column it has a bed depth of only a few centimetres. Studies have shown that carbon tested in this manner has the same adsorptive

capacity to that of the original carbon grains (Oxenford and Jykins Jr, 1991). Advantages in the use of small-scale column tests include assessment of adsorption capacity and kinetics, low capital and operational costs and the elimination of the need for numerical models. These initial investigations were designed to assess the adsorption kinetics of GAC and provide design data for the proposed pilot plant. 160 litres of feed water was spiked with 50ml of unleaded fuel and stirred to ensure thorough mixing. 1-2mm GAC was crushed and sieved, retaining the 0.165mm fraction. The RCT column was packed with 0.75g of the powdered carbon giving a bed depth of approximately 18mm. Flow rates were maintained at 5ml/min giving an empty bed contact time (EBCT) of approximately 20 seconds. EBCT is defined as the average time taken for a unit volume of feed water to pass through the bed volume of adsorbent when clean. Influent and effluent samples were taken every 24 hours. 40ml sample volumes were collected in sample vials. The samples were analysed on a Fisons 8000 series gas chromatograph, interfaced to a MD 800 quadropole mass spectrometer. A Tekmar 3000 Purge and Trap (P&T) system using a Precept II autosampler was used as the sample introduction method. Six compounds were quantified according to the USEPA 524.2 method for the analysis of volatile compounds; MTBE, Benzene, Toluene, Ethylbenzene, o/*m*-Xylene & *p*-Xylene. These compounds were chosen since they represent the compounds most likely to reach a PWS borehole after a fuel oil spillage.

Experimental Results and Discussion.

The GAC removal of MTBE and Benzene are illustrated in Figures 1 & 2 below.

Figure 1. Concentration of MTBE vs Time.

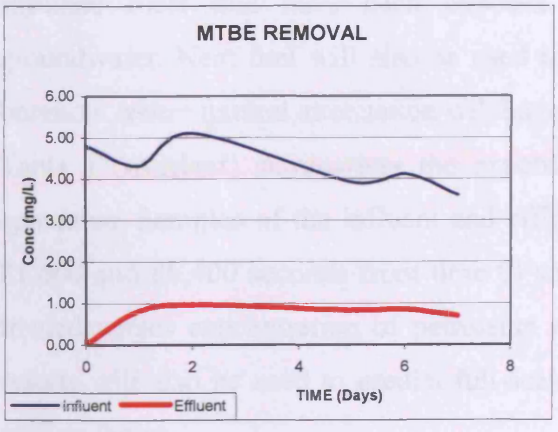
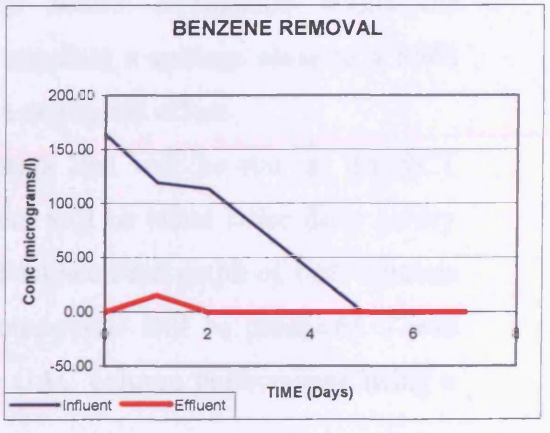


Figure 2. Concentration of Benzene vs Time.



The influent concentration of MTBE and benzene can be seen to fall over the 7-day period of the test. The concentration of benzene in the influent dropped to zero within 5 days. The drop in feed water concentration was believed to be due to volatilisation of the petroleum compounds in the feed water storage tanks and loss to the atmosphere To overcome this, the apparatus was modified to include floating lids and cooling to 12°C using a water refrigeration unit. A circulating pump was fitted to ensure adequate mixing. The modified RCT apparatus is illustrated in Figure 3 overleaf.

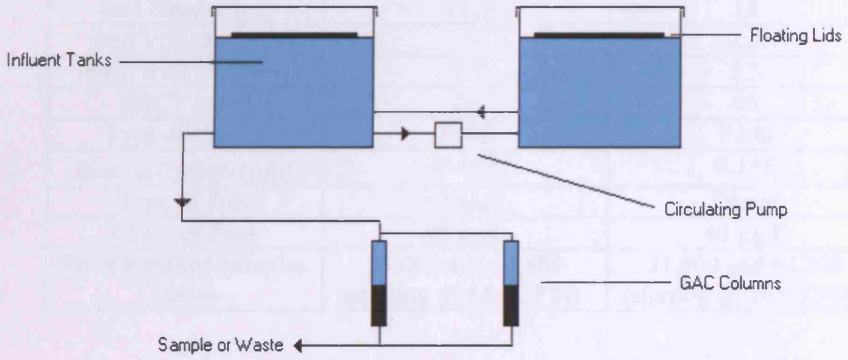


Figure 3. Modified RCT apparatus.

RCT Experimental Program.

Field samples of fuel oils will be collected and analysed on the GC-MS. From these results, a weathered synthetic fuel mix will be formulated and used to simulate fuels that have been exposed to natural attenuation within the groundwater. Neat fuel will also be used to simulate a spillage close to a PWS borehole where natural attenuation will have a negligible effect.

Table 1 (overleaf) summarises the experiments that will be run on the RCT apparatus. Samples of the influent and effluent will be taken twice daily (every 21,600 and 86,400 seconds from time 0) and an accurate graph of bed volumes treated verses concentration of petroleum compounds will be produced. These results will also be used to predict full-scale GAC column performance using a scaling factor.

The initial tests will assess GAC removal of diesel fuel at a concentration of 40µg/L to reflect past contamination events. Future tests will assess the capacity for GAC and other adsorbents to remove different fuel types such as unleaded gasoline, central heating fuel oil and aviation fuel at trace concentrations.

Table-1. RCT tests 1 & 2 operating conditions.

Test	1	2
Wt of Carbon (g)	0.5	0.75
Bed Depth (mm)	12.5	18
Bed Volume (ml^3)	1.0	1.5
Flow Rate (ml/min)	2.5	2.5
EBCT (secs)	25	40
Type of Carbon	F400	F400
Size of Carbon (µm)	0.165	0.165
Type of Fuel	Diesel	Diesel
Conc. of Fuel	40 µg/L	40 µg/L
Time Between Samples (secs)	21,000 and 64,800 (starting @ 16:00 PM).	21,000 and 64,800 (starting @ 16:00 PM).

Design of Modular Pilot Plant.

The second phase of the project will involve the construction and testing of a modular, pilot plant treatment system. This will include air stripping followed by 2 GAC columns. Capacity for advanced oxidation using hydrogen peroxide and *UV* will be included in the design.

The key design features for this system are:

- Air stripper designed for varied air:water ratios (2.2-150), and can be run on its own or followed by GAC columns.
- GAC columns can be run in series or parallel, with or without air-strip.
- Capacity for in line advanced oxidation using peroxide/*UV*.
- Flexible design to vary the system operating parameters to reflect different scenarios.

A schematic illustration of the modular pilot plant is shown in Figure 4 overleaf.

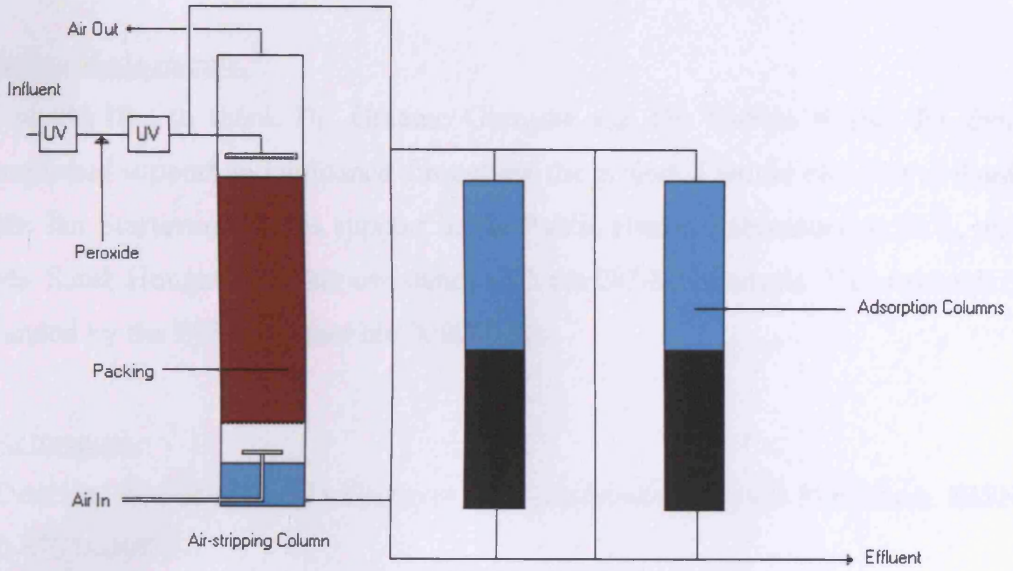


Figure 4. Modular pilot plant design

Conclusions.

- The introduction of new drinking water standards to the UK in 2003 will bring the issue of organic contamination of groundwaters to the fore.
- Benzene will be assigned a new standard of 1.0µg/L. Organic compounds such as MTBE, toluene, ethylbenzene and xylene are detectable in water at low concentrations but do not have limits assigned.
- The need for a 'rapid response' modular post abstraction remediation system for the removal of fuel oil compounds from potable groundwater sources has been identified.
- Early results suggest that a combination of advanced oxidation, air-stripping and adsorption will provide the most economical and practical solution.
- Further RCT and pilot plant results & analysis will be presented in a future paper.

Acknowledgements.

I would like to thank Dr. Graeme Glasgow and Dr. Debbie Squire for their continued support and guidance throughout the project. I would also like to thank Mr. Ian Sturtevant for his support in the Public Health Laboratory at UCL, and Ms. Sarah Houghton for her assistance with the GC-MS analysis. This research is funded by the EPSRC (grant no. 00800074).

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